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Industrial Process Profiles for Environmental Use: Chapter 29 Primary Copper Industry

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16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study.

The primary copper industry as defined for this study consists of mining, beneficiation, smelting, and refining. A profile of the industry is given including plant locations, capacities, and various statistics regarding production and consumption of copper, co-products, and by-products. The report summarizes the various commercial routes practiced domestically for copper production in a series of process flow diagrams and detailed process descriptions. Each process description includes available data regarding input materials, operating conditions, energy and utility requirements, waste streams produced (air, water, and solid waste), and control technology practices and problems.

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Primary Copper Industry

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INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE:
CHAPTER 29
PRIMARY COPPER INDUSTRY

by

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COPPER INDUSTRY

INDUSTRY DESCRIPTION

Many changes have recently been taking place in the primary copper industry. There is much speculation as to the direction these changes will or should take. Whether the trend is toward improved pyrometallurgical processing or toward adoption of hydrometallurgy, most experts agree that some basic changes are imminent.

At six smelters, copper has been or is now routinely produced by technologies newly introduced into U.S. production practice. One new smelter now uses a continuous flash smelting process and a continuous smelting process is being used to produce copper in Utah. One installation has produced copper with a roast-leach-electrowinning technique. Three advanced hydrometallurgical processes are approaching semicommercial production. The following description of the industry does not concentrate on these installations, since they do not now account for a sizable percentage of copper being produced.

Most copper production is now being accomplished with the "conventional" pyrometallurgical methods that center on the energy-inefficient reverberatory furnace. Matte from the reverberatory furnace is converted to blister copper, and the blister copper is reduced, cast into anodes, and refined in electrolytic cells. These operations occur in about 25 locations, all but five of which were operating before World War II. In twelve of these locations, copper has been produced since before World War I. Although new equipment was provided during the intervening years, in most of the plants, new technology was not. Most domestic copper is being made now by the same procedures used 50 years ago.

Raw Materials

The principal raw materials for copper production are the domestic ores, which consist of copper minerals embedded in gangue rock. Throughout the world, copper in minerals is most often chemically combined with sulfur, frequently with iron or arsenic, and sometimes with other elements. Table 1 shows five of these sulfide minerals; the first three listed are most abundant in the ores of this country.

When sulfide minerals are exposed to air and water, they oxidize to form sulfuric acid and metal ions. The metal ion may, in turn, react with rock minerals to form metal oxides, or they may move with ground or surface waters

Table 1. COPPER MINERALS IMPORTANT IN U.S. PRODUCTION (1)

Mineral	Composition	Copper content, percent weight	Occurrence[a]
Sulfide Ores			
Chalcopyrite	$CuFeS_2$	35	SW, NW, NC
Chalcocite	Cu_2S	80	SW, NW, NC
Bornite	Cu_5FeS_4	63	SW, NW
Covellite	CuS	66	SW, NW
Enargite	Cu_3AsS_4	48	NW
Oxide Ores			
Malachite	$CuCO_3 \cdot Cu(OH)_2$	57	SW, NW
Azurite	$2\ CuCO_3 \cdot Cu(OH)_2$	55	SW, NW
Cuprite	Cu_2O	89	SW
Chrysocolla	$CuSiO_3 \cdot 2H_2O$	36	SW
Native Copper	Cu	100	NC, SW

[a] NW - Montana and surrounding area.
NC - Michigan and surrounding area.
SW - Arizona and surrounding area.

and subsequently precipitate to form secondary metal deposits. Weathering may therefore create deposits of oxidized copper minerals. The table shows four of these, the highly colored azurite and malachite being most abundant in domestic ores.

The ore deposits of northern Michigan are a unique occurrence of primary origin, and native copper mixed with sulfide minerals is mined in this area. Table 2 gives an analysis of the ore from this deposit. Except for the presence of elemental copper and the low-sulfur content, this analysis is similar to that of most domestic ores, since it shows iron present in much higher concentration than copper in a gangue rock of silica and alumina minerals.

The first step in the processing of an ore is to form a copper concentrate, which consists of the copper minerals separated from most of the gangue. These concentrates are an article of commerce, and represent another raw material of this industry. Ores mined primarily for other metals may be the origin of concentrates rich in copper, which are sold to copper producers. This may constitute 5 to 10 percent of all the primary copper that is mined in this country. Also concentrates are regularly imported from other countries; domestic smelters frequently process concentrates from Canada, South America, Australia, and the Phillippines.

The industry also imports copper from other countries at several intermediate stages of processing. These imports include partially smelted matte and crude anode or blister copper. Although they do not represent a large fraction of the copper consumed in this country, most copper imports are in the form of these intermediate products. A small amount of unprocessed high-grade ore is also imported.

The industry consumes other materials in various processing steps, but not in large quantities. Mining and concentrating entail use of explosives and small amounts of organic chemicals, and smelting requires limestone and silica rock as fluxing materials.

Primary copper smelting and refining, together with the primary aluminum industry, accounts for 3 percent of all energy consumed by manufacturing industries in the U.S. (2). Currently, natural gas is the fuel most heavily relied upon by copper smelters, with oil also being widely used. Energy consumption in 1974 for all copper refining and smelting operations in the U.S. was: natural gas - 1.52×10^{13} kilocalories, oil - 4.13×10^{12} kilocalories, and electricity - 6.82×10^{8} kilowatt-hours (2). Coal was originally the only fuel source in the domestic copper industry, but its use was largely discontinued in favor of oil, natural gas, or electricity because of material handling problems. However, the rapidly increasing costs of these forms of energy is leading to new consideration of reconversion to coal.

Products

Commerce recognizes a number of different grades of copper, classified into two main groups. Relatively impure grades are directly produced in a copper smelter. These are sold for use in alloys or for other special purposes, or they may be exported to be refined elsewhere. More than 90 percent

TABLE 2. TYPICAL ANALYSIS OF COPPER ORE USED AT COPPER RANGE COMPANY, WHITE PINE, MICHIGAN

Element	Percentage (Weight)
Cu	1.0
Ag	0.0006
Au	Trace
Al_2O_3	15.0
SiO_2	61.5
CaO	7.4
Fe	6.6
MgO	3.7
Ni	0.005
S	0.35
Pb	0.001
As	0.0005
Mo	0.002
Bi	0.0001
Mn	0.05
Zn	0.001
Na	1.5
K	1.0
Co	0.003
Se	0.0005

of the copper produced is refined in this country into one of the electrolytic grades. Table 3 shows the distribution of consumption of electrolytic copper in 1978. More than two-thirds of it is used directly to manufacture wire and tubing. More than half the electrolytic copper is cast at the refinery into wirebars for direct use on wire and tubing forming machines.

Several byproduct elements are isolated from copper ores. In 1978 the copper industry produced all the arsenic, selenium, and tellurium manufactured in this country, almost all the platinum and palladium, and almost half the gold, silver, and molybdenum. Except for molybdenum, all of these were produced as purified metals or compounds. Molybdenum was sold as concentrate, and most copper producers also reclaim zinc and lead as a concentrate. Several copper smelters recover tellurium, and one company situated near steel mills makes a high-grade iron sinter from the iron pyrite in its ore. This same company manufactures sulfuric acid as a major product, and most others have facilities to manufacture it as a byproduct. Three companies produce copper sulfate, and two manufacture chemicals of a specialized nature in the same plant with their copper operations.

Table 4 provides the basic 1978 statistics of this industry, and Table 5 lists major sulfuric acid producers.

Companies

The United States is the world's largest copper producer, accounting for about 18 percent of the total world mine production in 1978. Domestic mine output that year was estimated at 1.36 million metric tons and valued at $1.97 billion (4).

In 1978 nine companies operated 16 primary smelters and 19 companies operated 23 refineries and electrowinning plants (4). The locations of domestic primary copper smelters and refineries are indicated in Figure 1. Table 6 lists some of these companies, with applicable data. The three largest domestic producers are Kennecott Copper Corporation, Phelps-Dodge Corporation, and ASARCO, Inc.

Most of these companies own or control domestic mines that supply at least part of their own needs. Table 7 lists the 25 largest copper mines operating in 1976. Most of these were directly owned by a producing company. At least three other large companies own mines or leaching operations intended primarily for production of copper, as do several smaller companies. The 25 listed mines produced more than 95 percent of the domestic copper in 1974. The remaining five percent of domestic copper was produced from a few smaller mines, or as byproducts of other mining industries.

Projected changes through 1985 include addition of new capacity and improvement of pollution control. Technology should not change radically due to the lead time required, the lack of recent innovations, and the capital intensive nature of the industry (2).

TABLE 3. CONSUMPTION OF REFINED COPPER IN 1978 (3)

Consumer	Quantity, metric tons
Wire mills	1,514,489
Brass mills	619,278
Secondary smelters	3,546
Chemical plants, foundries, and miscellaneous plants	32,659[a]

[a] Estimated.

TABLE 4. STATISTICAL DATA FOR THE PRIMARY COPPER INDUSTRY IN THE UNITED STATES IN 1978 (3)

Primary copper produced, metric tons	
Mines, from domestic ores	1,351,956
Smelters, from domestic ores	1,270,002
Refineries, from domestic ores	1,278,129
Refineries, from foreign ore, matte, etc.	112,720
Exports, metric tons	
Unmanufactured	177,847
Refined	91,924
Imports, metric tons	
Unmanufactured	546,401
Refined	414,703

TABLE 5. PRINCIPAL BY-PRODUCT SULFURIC ACID PRODUCERS - 1974 (5)

Producer	Capacity, metric ton/year
The Anaconda Co.	
Anaconda, Montana	210,000
ASARCO, Inc.	
Corpus Christi, Texas	104,000[a]
El Paso, Texas	145,000
Hayden, Arizona	163,000
Tacoma, Washington	49,000
Cities Service Co.	
Copperhill, Tennessee	1,143,000[b]
Inspiration Consolidated Copper Co.	
Inspiration, Arizona	397,000
Kennecott Copper Corp.	
Hurley, New Mexico	181,000
Hayden, Arizona	249,000
Garfield, Utah	544,000
Magma Copper Co.	
San Manuel, Arizona	803,000
Phelps Dodge Corp.	
Ajo, Arizona	91,000
Hidalgo, New Mexico	524,000
Morenci, Arizona	544,000

[a] ASARCO - Corpus Christi smelter is no longer operating.

[b] Approximate composition is 5% smelter gases; 95% gases from pyrites.

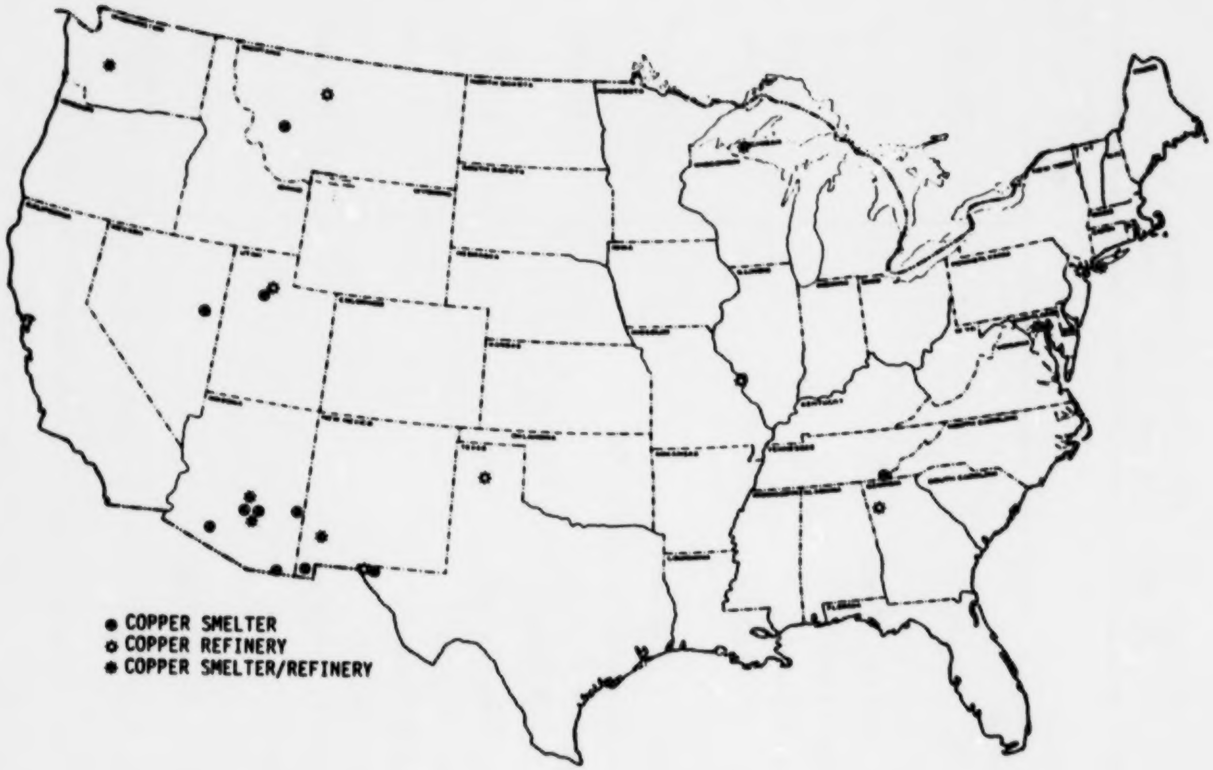
● COPPER SMELTER
○ COPPER REFINERY
● COPPER SMELTER/REFINERY

Figure 1. Primary U.S. copper smelting and refining locations.

TABLE 6. U.S. PRIMARY COPPER PRODUCERS (6,7)

Company	Location	Description	Capacity, metric ton/year (Cu content)
AMAX, Inc.	Cateret, New Jersey	Refinery	236,000
The Anaconda Company (ARCO)	Anaconda, Montana	Smelter	180,000
	Great Falls, Montana	Refinery	229,000
ASARCO, Inc.	Tacoma, Washington	Smelter/refinery	91,000/142,000
	El Paso, Texas	Smelter	104,000
	Hayden, Arizona	Smelter	163,000
	Amarillo, Texas	Refinery	381,000
Cerro Corporation	St, Louis, Missouri	Refinery	236,000
Cities Service Company	Copperhill, Tennessee	Smelter	20,000
Copper Range Company (Louisiana Land)	White Pine, Michigan	Smelter/refinery	82,000/82,000
Inspiration Consolidated Copper Company	Miami, Arizona	Smelter/refinery	64,000/136,000
Kennecott Copper Corporation	Garfield, Utah	Smelter	245,000
	Hurley, New Mexico	Smelter/refinery	73,000/93,000
	Hayden, Arizona	Smelter	73,000
	McGill, Nevada	Smelter	45,000
	Baltimore, Maryland	Refinery	250,000
	Magna, Utah	Refinery	169,000
Magma Copper Company (Newmont Mining)	San Manuel, Arizona	Smelter/refinery	181,000/181,000
Phelps Dodge Corporation	Morenci, Arizona	Smelter	161,000
	Douglas, Arizona	Smelter	115,000
	Hidalgo, New Mexico	Smelter	91,000
	Ajo, Arizona	Smelter	64,000
	El Paso, Texas	Refinery	404,000
	Laurel Hill, New York	Refinery	83,000
Southwire Company	Carrollton, Georgia	Refinery	65,000

Note: Refineries typically produce copper from both blister and scrap in varying proportions, and for this reason the U.S. Bureau of Mines does not categorize refineries as either "primary" or "secondary." In general, refineries located in Western states or adjacent to primary smelters process chiefly a blister feed, while those refineries in the East produce a higher proportion of copper from scrap.

TABLE 7. TWENTY-FIVE LEADING COPPER-PRODUCING MINES IN THE UNITED STATES IN 1976, IN ORDER OF OUTPUT (8)

Rank	Mine	County and State	Operator	Source of Copper
1	Utah Copper	Salt Lake, Utah	Kennecott Copper Corporation	Copper ore, copper precipitates
2	Morenci	Greenlee, Arizona	Phelps Dodge Corporation	Copper ore, copper precipitates, copper tailings
3	San Manuel	Pinal, Arizona	Magma Copper Company	Copper ore
4	Sierrita	Pima, Arizona	Duval Sierrita Corporation	Do.
5	Twin Buttes	do	Anamax Mining Company	Do.
6	Tyrone	Grant, New Mexico	Phelps Dodge Corporation	Copper ore, copper precipitates
7	Berkeley Pit	Silver Bow, Montana	The Anaconda Company	Do.
8	Ray Pit	Pinal, Arizona	Kennecott Copper Corporation	Do.
9	Pima	Pima, Arizona	Cyprus Pima Mining Company	Copper ore
10	Metcalf	Greenlee, Arizona	Phelps Dodge Corporation	Copper ore, copper tailings
11	Pinto Valley	Gila, Arizona	Cities Service Company	Copper ore, copper precipitates
12	Chino	Grant, New Mexico	Kennecott Copper Corporation	Do.
13	New Cornelia	Pima, Arizona	Phelps Dodge Corporation	Copper ore

(continued)

TABLE 7 (continued)

Rank	Mine	County and State	Operator	Source of Copper
14	White Pine	Ontonagon, Michigan	White Pine Copper Company	Do.
15	Magma	Pinal, Arizona	Magma Copper Company	Do.
16	Inspiration	Gila, Arizona	Inspiration Consolidated Copper Company	Copper ore, copper precipitates
17	Mission	Pima, Arizona	ASARCO Inc.	Copper ore
18	Yerrington	Lyon, Nevada	The Anaconda Company	Copper ore, copper precipitates
19	Continental	Grant, New Mexico	UV Industries, Inc.	Do.
20	Silver Bell	Pima, Arizona	ASARCO, Inc.	Do.
21	Sacaton Unit	Pinal, Arizona	do.	Copper ore
22	Bagdad	Yavapai, Arizona	Cyprus Bagdad Copper Company	Do.
23	Lakeshore	Pinal, Arizona	Hecla Mining Company	Do.
24	Eaperanza	Pima, Arizona	Duval Corporation	Copper ore, copper precipitates
25	Copper Canyon	Lander, Nevada	do.	Do.

An estimated 40,000 persons are employed by the primary copper industry. Most are engaged in mining and concentrating. In 1974, industry employment was reported as 33,942 persons, of which 14,861 were in open-pit mines, 9,545 in underground mines, and 4,536 in ore concentrating mills. The copper industry is the largest single employer in Arizona, Montana, Nevada, and Utah.

Environmental Impacts

Smelting is the most important source of environmental problems in the copper industry.

Emissions of air pollutants from copper processing are of concern, especially those that are potentially hazardous to human health. Among the known trace elements of concern are arsenic and cadmium. The copper industry is a primary source of arsenic emissions, producing about 30 percent of total arsenic emissions in the United States.

Copper smelters are a major source of sulfur dioxide, emitting 80 percent of the total amount of SO_2 emitted from the copper, lead, and zinc industries. The industry is implementing control methods to recover some of the SO_2 as a marketable product. Fifteen percent of the SO_2 generated by the industry is fugitive emissions.

The industry makes use of water recycle techniques, but the extent has not been quantified. Mine wastewater may contain acid and dissolved metals. Mill tailings may also contain heavy metals. Smelter and refining wastes often contribute a heavy load of dissolved metals to the tailings pond. These wastes can affect the quality of the decant water as well as effluent volumes. Slag from the industry, which is dumped, contains many elements. Table 8 presents approximate quantities of selected pollutants from the U.S. primary copper industry (9). Primary copper smelting and fire refining produce approximately 3 metric tons of wastes containing slag, sludge, and dust (including acid plant sludge) per metric ton of product. Smelting followed by electrolytic refining produces about 2.4 kilograms of wastes per metric ton of product.

In 1974 the copper ore mining and concentrating industry produced about 651 million metric tons of solid waste, or about 85 percent of the national total for metals mining and concentrating. Of this figure, 56 percent was waste rock, 7 percent was overburden, and 36 percent was concentrator tailings (7).

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TABLE 8. ANNUAL GENERATION OF SELECTED POLLUTANTS FROM U.S. PRIMARY COPPER INDUSTRY - 1978 (9)
(metric tons)

	Production	Particulate emissions		Sulfur oxide emissions	
		Before control	After control	Before control	After control
Ore crushing	269,000,000	269,400	269,400	-	-
Roasting	2,781,000	75,400	14,300	634,000	N.A.
Smelting	5,562,000	122,400	17,100	962,100	N.A.
Converting	5,562,000	124,000	18,600	1,957,800	N.A.
Refining	5,562,000	29,200	4,100	-	-
Total	-	620,400	323,500	3,553,900	1,930,400

N.A. - Not available.

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INDUSTRY ANALYSIS

The environmental impacts of many industries, including the primary copper industry, have received wide attention and have been the subject of many industrial and governmental studies. Emissions of SO_2 and their impacts on the atmosphere are considered especially important.

This industry analysis examines each individual production operation, called here a process, to examine in detail its purpose and its actual or potential effect on the environment. Each process is examined in the following aspects:

1. Function
2. Input materials
3. Operating conditions
4. Utilities
5. Waste streams
6. Control technology
7. EPA classification code
8. References

The only processes included in this section are those that are either operating in the United States, are under construction, or are currently being demonstrated on a large scale at a U.S. facility. Figure 2 is a flowsheet showing these processes, their interrelationships, and their major waste streams.

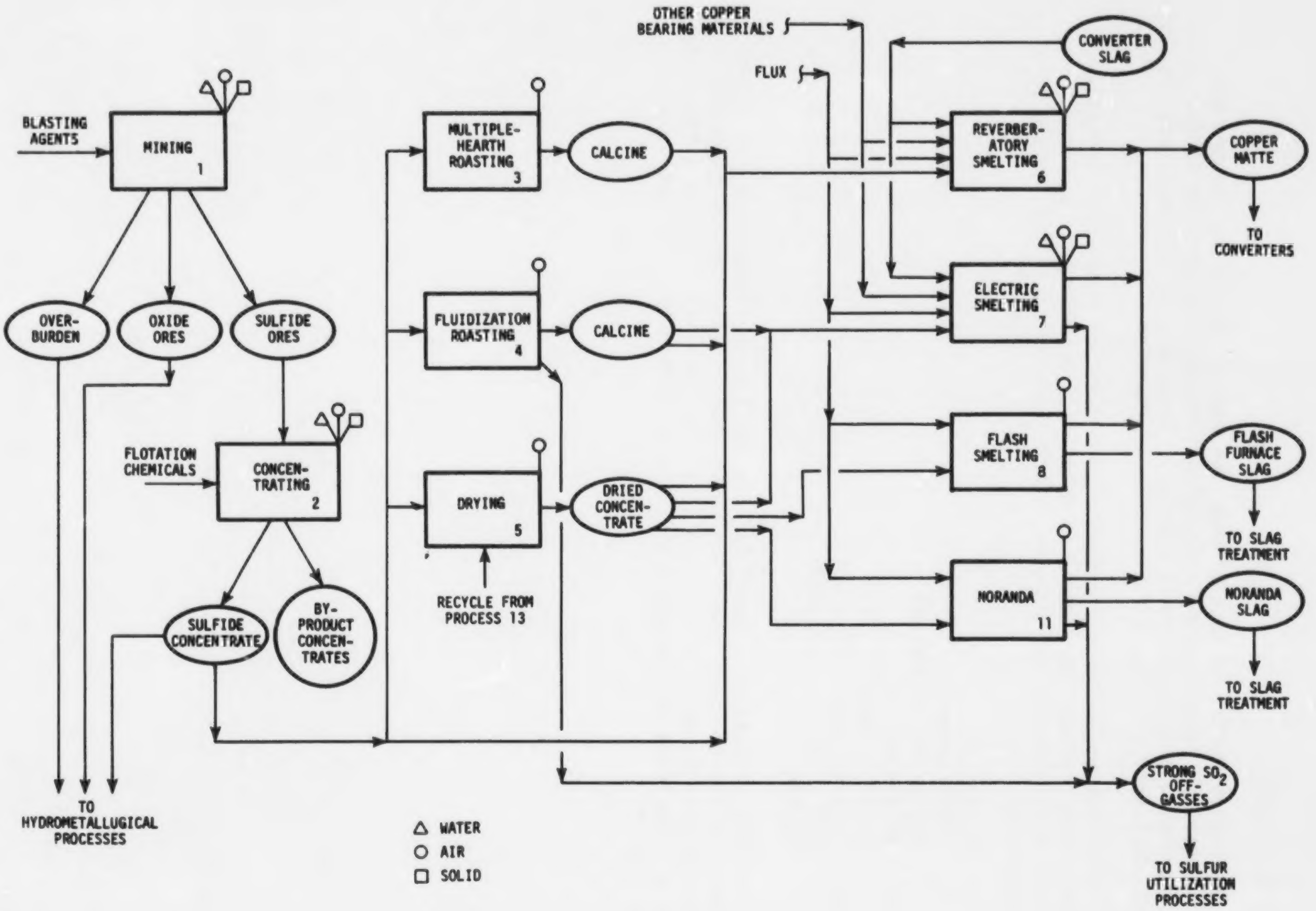
BLASTING AGENTS
MINING 1
OVER-BURDEN
OXIDE ORES
SULFIDE ORES
FLOTATION CHEMICALS
CONCEN-TRATING 2
SULFIDE CONCENTRATE
BY-PRODUCT CONCEN-TRATES
TO HYDROMETALLUGICAL PROCESSES
MULTIPLE-HEARTH ROASTING 3
FLUIDIZATION ROASTING 4
DRYING 5
RECYCLE FROM PROCESS 13
CALCINE
CALCINE
DRIED CONCEN-TRATE
OTHER COPPER BEARING MATERIALS
FLUX
CONVERTER SLAG
REVERBER-ATORY SMELTING 6
ELECTRIC SMELTING 7
FLASH SMELTING 8
NORANDA 11
COPPER MATTE
TO CONVERTERS
FLASH FURNACE SLAG
TO SLAG TREATMENT
NORANDA SLAG
TO SLAG TREATMENT
STRONG SO_2 OFF-GASSES
TO SULFUR UTILIZATION PROCESSES
△ WATER
○ AIR
□ SOLID

Figure 2. Copper industry flow sheet.

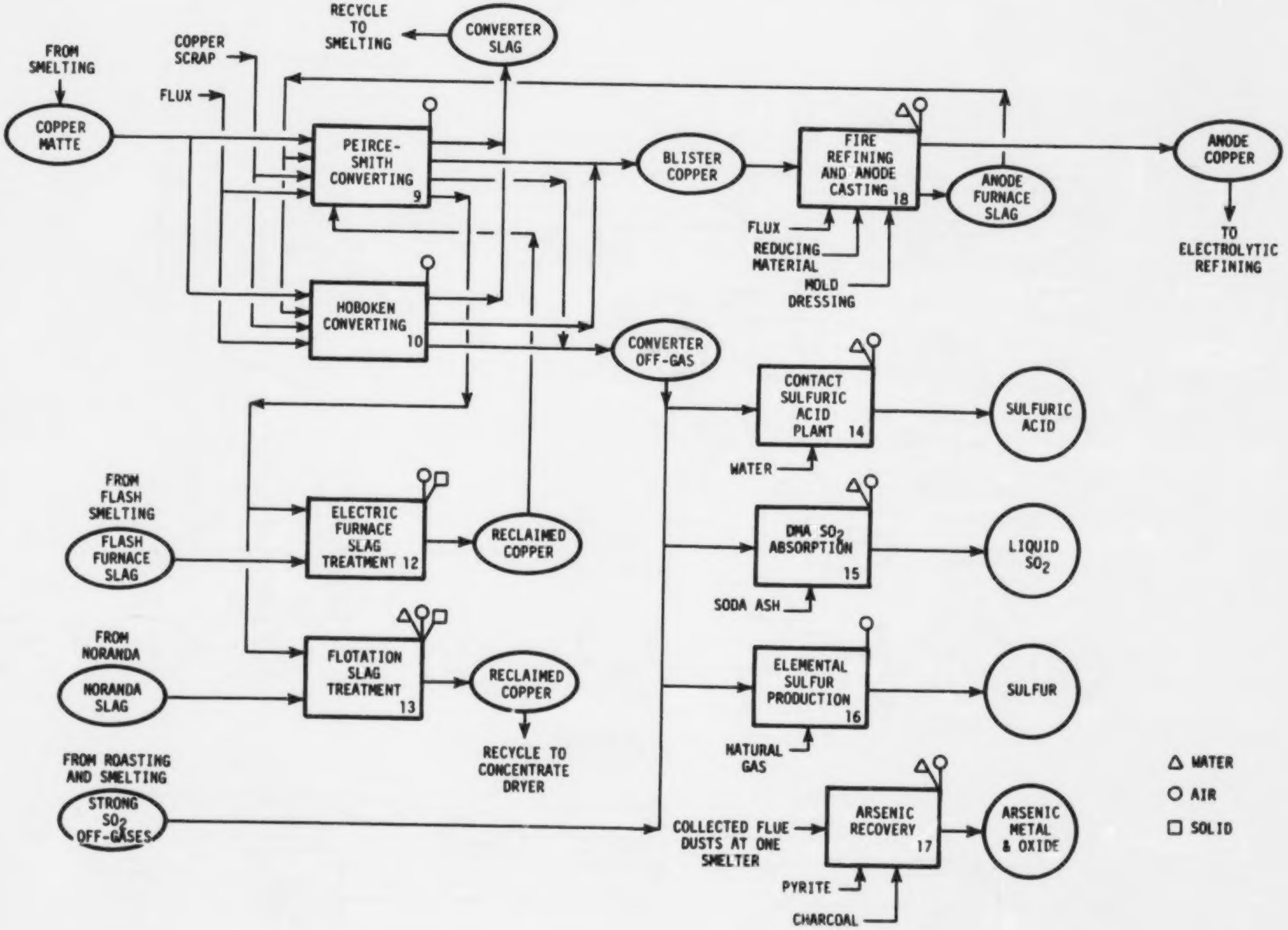
FROM SMELTING
COPPER MATTE
COPPER SCRAP
FLUX
RECYCLE TO SMELTING
CONVERTER SLAG
PEIRCE-SMITH CONVERTING 9
HOBOKEN CONVERTING 10
BLISTER COPPER
FIRE REFINING AND ANODE CASTING 18
ANODE FURNACE SLAG
ANODE COPPER
TO ELECTROLYTIC REFINING
FLUX
REDUCING MATERIAL
MOLD DRESSING
CONVERTER OFF-GAS
CONTACT SULFURIC ACID PLANT 14
SULFURIC ACID
WATER
DMA SO_2 ABSORPTION 15
LIQUID SO_2
SODA ASH
ELEMENTAL SULFUR PRODUCTION 16
SULFUR
NATURAL GAS
ARSENIC RECOVERY 17
ARSENIC METAL & OXIDE
COLLECTED FLUE DUSTS AT ONE SMELTER
PYRITE
CHARCOAL
FROM FLASH SMELTING
FLASH FURNACE SLAG
ELECTRIC FURNACE SLAG TREATMENT 12
RECLAIMED COPPER
FROM NORANDA
NORANDA SLAG
FLOTATION SLAG TREATMENT 13
RECLAIMED COPPER
RECYCLE TO CONCENTRATE DRYER
FROM ROASTING AND SMELTING
STRONG SO_2 OFF-GASES
△ WATER
○ AIR
□ SOLID

Figure 2 (continued)

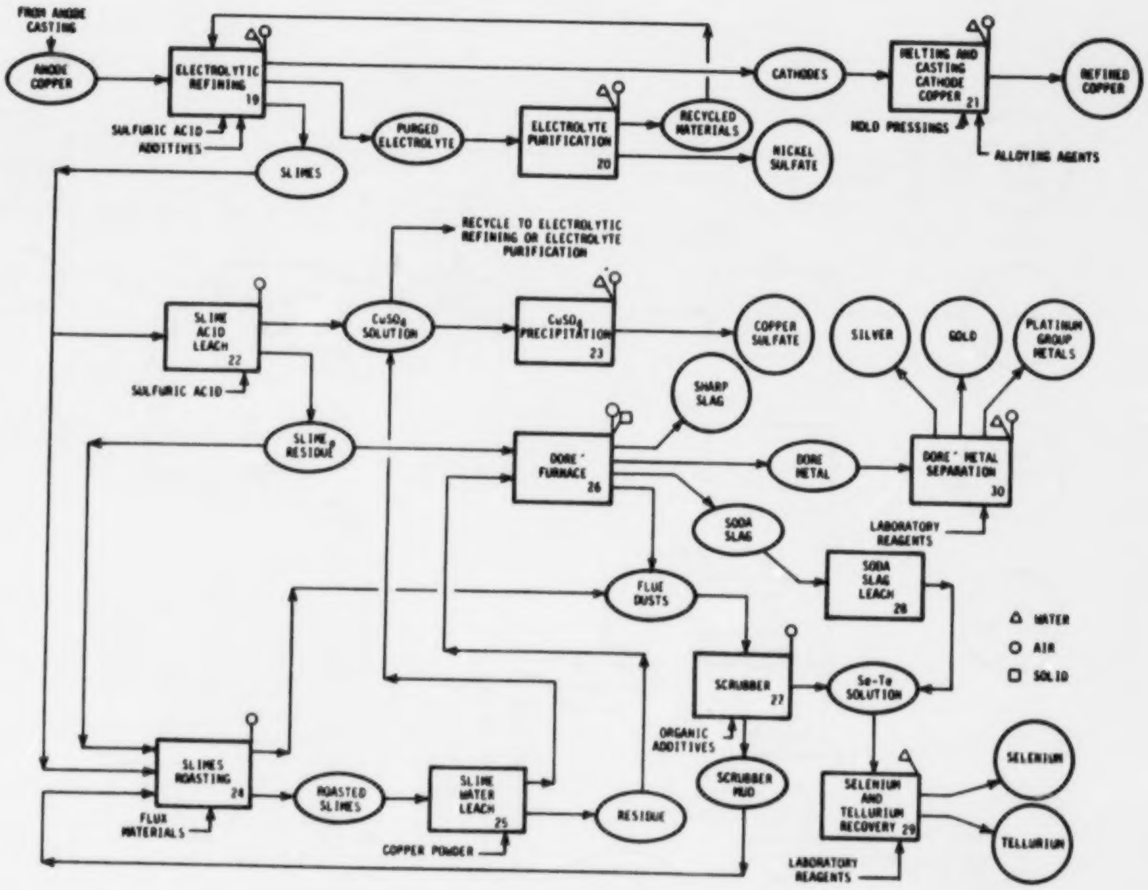
FROM ANODE CASTING
ANODE COPPER
ELECTROLYTIC REFINING 19
SULFURIC ACID
ADDITIVES
SLIMES
PURGED ELECTROLYTE
ELECTROLYTE PURIFICATION 20
RECYCLED MATERIALS
NICKEL SULFATE
CATHODES
MELTING AND CASTING CATHODE COPPER 21
MOLD PRESSINGS
ALLOYING AGENTS
REFINED COPPER
RECYCLE TO ELECTROLYTIC REFINING OR ELECTROLYTE PURIFICATION
SLIME ACID LEACH 22
SULFURIC ACID
CuSO4 SOLUTION
CuSO4 PRECIPITATION 23
COPPER SULFATE
SLIME RESIDUE
DORE' FURNACE 26
SHARP SLAG
DORE METAL
DORE' METAL SEPARATION 30
SILVER
GOLD
PLATINUM GROUP METALS
LABORATORY REAGENTS
SODA SLAG
SODA SLAG LEACH 28
FLUE DUSTS
SCRUBBER 27
ORGANIC ADDITIVES
SCRUBBER MUD
Se-Te SOLUTION
SELENIUM AND TELLURIUM RECOVERY 29
LABORATORY REAGENTS
SELENIUM
TELLURIUM
SLIMES ROASTING 24
FLUX MATERIALS
ROASTED SLIMES
SLIME WATER LEACH 25
COPPER POWDER
RESIDUE
△ WATER
○ AIR
□ SOLID

Figure 2 (continued)

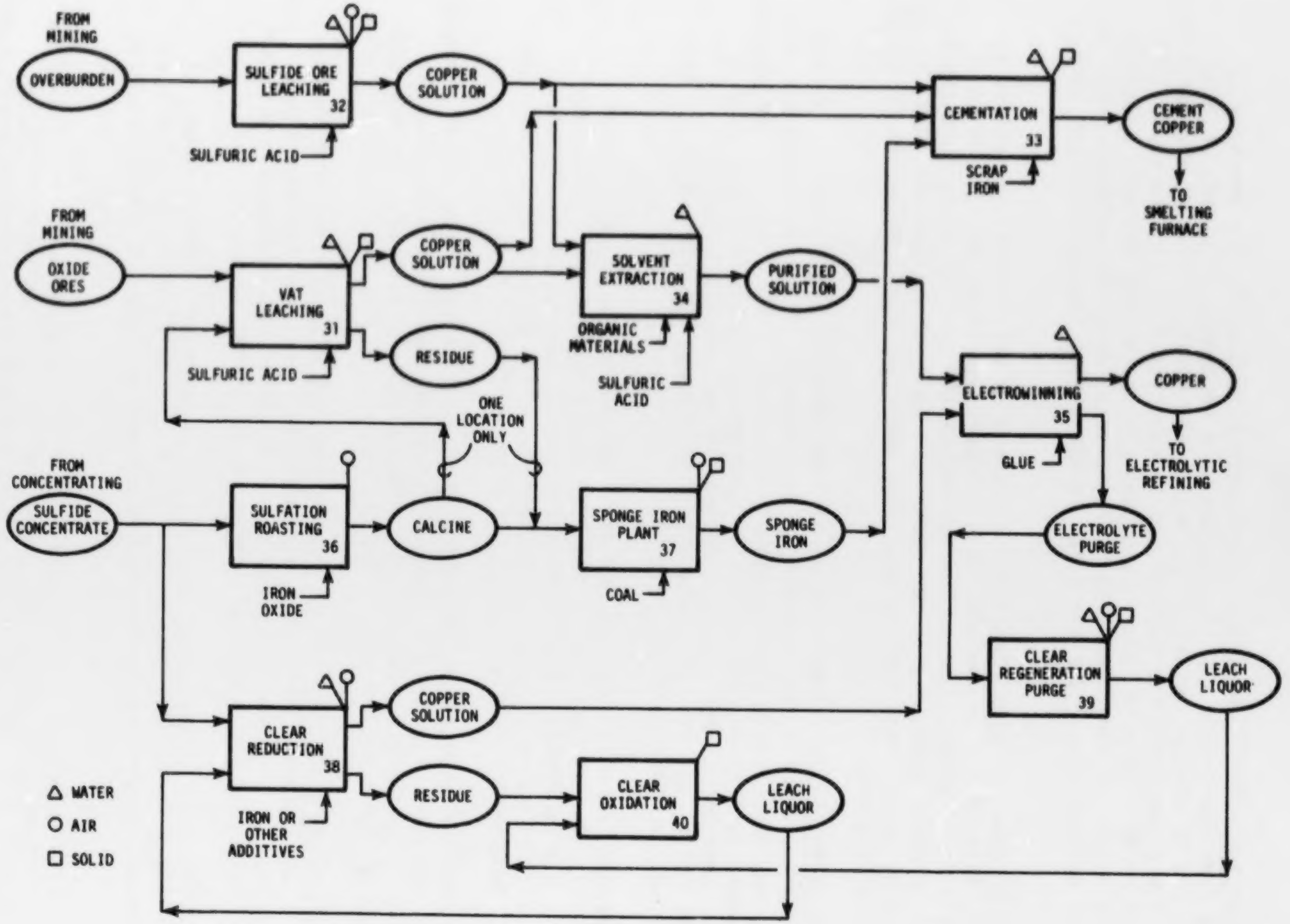
FROM MINING
OVERBURDEN
SULFIDE ORE LEACHING 32
SULFURIC ACID
COPPER SOLUTION
CEMENTATION 33
SCRAP IRON
CEMENT COPPER
TO SMELTING FURNACE
FROM MINING
OXIDE ORES
VAT LEACHING 31
SULFURIC ACID
COPPER SOLUTION
RESIDUE
SOLVENT EXTRACTION 34
ORGANIC MATERIALS
SULFURIC ACID
PURIFIED SOLUTION
ELECTROWINNING 35
GLUE
COPPER
TO ELECTROLYTIC REFINING
ONE LOCATION ONLY
FROM CONCENTRATING
SULFIDE CONCENTRATE
SULFATION ROASTING 36
IRON OXIDE
CALCINE
SPONGE IRON PLANT 37
COAL
SPONGE IRON
ELECTROLYTE PURGE
CLEAR REGENERATION PURGE 39
LEACH LIQUOR
CLEAR REDUCTION 38
IRON OR OTHER ADDITIVES
COPPER SOLUTION
RESIDUE
CLEAR OXIDATION 40
LEACH LIQUOR
△ WATER
○ AIR
□ SOLID

Figure 2 (continued)

Mining

1. Function - Rock containing enough copper to justify its recovery is removed from the ground and transported to a concentrator plant. Mining methods are determined by the size, depth, and configuration of the ore body, as these are adaptable for underground or open pit mining. The capability for high productivity in large-scale open pit operations has made possible the development of large deposits of relatively low-grade porphyry ores; in 1973, 83 percent of all the ore mined in the United States came from open pits (1).

In an open pit mine, holes for placement of explosives are drilled behind the face of a near-vertical bank. Other explosives are placed in secondary drill holes. The explosives reduce the rock to sizes that can be handled by power shovels or other mechanical equipment. Shovels load the ore into trucks or railroad cars or onto belt conveyors for transportation to the concentrator plant.

2. Input Materials - Important copper ore minerals are listed in Table 1. Chalcopyrite, bornite, and enargite are considered the primary minerals that were formed deep underground by igneous processes. The other sulfide minerals were formed by the leaching action of underground water in the absence of oxygen. When oxygen was present, the sulfur was oxidized, and minerals such as chrysocolla, azurite, and malachite were formed. Native copper is sometimes found in these oxidized deposits.

Porphyry deposits are now the major source of the world's copper. Porphyry is the term applied to the type of deposit in which the copper minerals are uniformly distributed throughout a rock composed of other minerals. The copper content is between 0.6 and 2 percent (2). The copper ores of southwestern United States are from porphyry deposits.

Explosives used in copper mining are almost always a mixture of ammonium nitrite and fuel oil (AN-FO). Some mines add sodium nitrate to make the explosive slightly more powerful (3). No values are available for the consumption of these explosives.

3. Operating Conditions - Most copper ores are mined in the arid regions of the West or Southwest where open pit operations continue through both hot and cold weather. Other mining operations in Michigan and Tennessee are underground mines where more constant temperatures prevail.

4. Utilities - In most mines, electrically operated power equipment is used for drilling, loading, and hauling. In 1973, 1.02 kilowatt-hours of electricity was consumed by the mining process per kilogram of copper produced (4).

A small amount of water is needed for equipment cooling, drill lubrication, dust control spraying, equipment washing, and sanitary facilities. Occasionally the water sent to the mine is reused water from the concentrator plant or tailings pond.

5. Waste Streams - Mining operations generate fairly large amounts of dust from drilling, blasting, loading, and transporting operations. One estimate of 110 grams of fugitive dust per metric ton of ore mined is given as the average for several types of nonferrous mining (5). The dust composition is dependent on the character of the ore being mined, and there is a large variation in particle size.

Wastewater from copper mining comes from seepage or runoff from the mine or spoil dumps, and from the water sent into the mine for utility uses. Improper backfill operations may result in acid drainage. The amount of wastewater from open pit copper mines ranges from zero to 0.3 cubic meter of water per metric ton of ore mined. From underground mines, the amount ranges from 0.008 to 4.0 cubic meter per metric ton of ore (6). Chemical characteristics are typical of those from any sulfide mine. Table 9 gives analyses of waters from two copper mines.

Large amounts of solid wastes are generated in a mining operation. Overburden stripped to uncover an ore body, shaft and tunnel developmental wastes, and low-grade ore (less than 0.4% copper) found within the mine are disposed of near the mine. The amount varies widely, from as little as 0.004 metric ton per metric ton of ore up to 15 metric tons per metric ton of ore mined. Average quantities in 1973 were reported as 2.65 metric tons per metric ton for open pit mines, and 0.13 metric ton per metric ton for underground mines (7). These wastes contain small and varying amounts of copper minerals, sometimes minerals of other metals, and large amounts of the native rock of the region. Concentrations of most materials do not exceed background levels (8).

6. Control Technology - The only control provided for fugitive dust is the manual use of water sprays, to be used when needed. Dust from blasting can be controlled by proper blast design. Most open pit copper mines are very large, with sufficient natural ventilation that dust conditions are not unbearable.

Mining companies attempt to locate waste dumps where natural seepage will not contaminate a stream or underground aquifer. Otherwise there is little control of these solid wastes in the copper industry (9).

Mine water wastes and seepage from the spoil dumps are major potential sources of water pollution from the primary copper industry. Two characteristics of copper mines differ from those in the lead and zinc industries. First, their location greatly simplifies control of water discharges. Most large open pit mines are in regions of deficient rainfall, and some are in desert areas. Natural evaporation within the pit greatly reduces the volume of wastes that must be pumped out, and seepage from spoil dumps rarely enters a stream. The water that accumulates is in many cases disposed of merely by pumping it onto a nearby flat area, where it either seeps into the alkaline soil or evaporates. It is thought that most of the dissolved metals are converted to insoluble compounds by this process, and officials of several mining companies state that they have shown that none of these waters has

TABLE 9. RAW WASTE LOAD IN WATER PUMPED FROM SELECTED COPPER MINES (7)

Parameter	Underground mine: Concentration (mg/ℓ)	Underground mine: Raw waste load per unit ore mined kg/1000 metric tons	Open-pit mine: Concentration (mg/ℓ)	Open-pit mine: Raw waste load per unit ore mined kg/1000 metric tons
Flow	3,815.3m^3/day	17.28 m^3/1000 metric tons	409 m^3/day	75 m^3/1000 metric tons
pH	7.37[a]	7.37[a]	6.96[a]	6.96[a]
TDS	29,250	5,053.9	1,350	101
TSS	69	11.9	2	0.2
Oil & grease	<1.0	<0.173	7	0.5
TOC	<4.5	<0.778	10	0.75
COD	819	141.5	4	0.3
B	2.19	0.378	0.07	0.005
Cu	0.87	0.150	1.05	0.08
Co	<0.04	<0.007	<0.06	<0.005
Se	<0.077	<0.013	0.096	0.007
Te	0.60	0.104	<0.2	<0.02
As	<0.07	<0.012	<0.01	<0.0008
Zn	2.8	0.484	0.1	0.008
Sb	<0.5	<0.086	<0.5	<0.04
Fe	<0.1	<0.017	<0.1	<0.008
Mn	2.22	0.384	0.9	0.07
Cd	<0.02	<0.003	<0.03	<0.002
Ni	<0.05	<0.009	<0.05	<0.004
Mo	<0.5	<0.086	<0.2	<0.02
Sr	119	20.6	0.8	0.06
Hg	<0.0001	<0.00002	<0.0001	<0.000008
Pb	<0.1	<0.017	<0.5	<0.04

[a] Value in pH units

entered underground supplies. In the vicinity of some of these mines, copper, zinc, selenium, and arsenic are detected in analysis of water from springs and wells, in concentrations usually less than 0.1 milligrams per liter; it is not clear whether this amount exceeds the natural concentrations in a highly mineralized region (1). These alkali waters naturally have total dissolved solids that can be several thousand milligrams per liter.

Near some copper mines, the practice of leaching low-grade ore is being practiced. This practice and its effect in the control of mining wastewaters is described in the section outlining Process No. 32, Sulfide Ore Leaching.

7. EPA Source Classification Code - None

8. References -

1. Mineral Facts and Problems, Washington, D.C. U.S. Department of the Interior, Bureau of Mines, 1970.

2. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency, Washington, D.C. September 1973.

3. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc., New York. 1967.

4. Energy Consumption in Domestic Primary Copper Production, U.S. Bureau of Mines.

5. Davis, W.E. National Inventory of Sources and Emissions: Copper, Selenium, and Zinc. PB-210 679, PB-210 478, and PB-210 677. U.S. Environmental Protection Agency. Research Traingle Park, North Carolina. May 1972.

6. Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry. Point Source Category Volumes I and II. EPA/1-75/032-6. Environmental Protection Agency, Washington, D.C. February 1975.

7. Minerals Yearbook. U.S. Department of the Interior, Bureau of Mines., Washington, D.C. 1973.

8. A Study of Waste Generation, Treatment and Disposal in the Metals Mining Industry. PB 261-052. Midwest Research Institute for Environmental Protection Agency. Washington, D.C. October 1976.

9. Dayton, S. The Quiet Revolution in the Wide World of Mineral Processing. Engineering and Mining Journal. June 1975.

Concentrating

1. Function - Sulfide ore from the mine is separated by the concentration process into two or more fractions. The fractions rich in valuable minerals are called concentrates, and the waste rock, low in metals content, is called the gangue. With this process, ore that usually contains less than 1 percent copper is concentrated into a fraction analyzing from 20 to 30 percent copper. At least 85 percent of the ore copper content is recovered in the concentrate.

Concentrating consists of milling the ore, crushing and grinding it to a fine powder, and then separating the minerals by froth flotation. In milling, the ore is sent through crushers and then through fine grinders. Between stages, the ore is classified (screened), and the final milled product is a mixture of particles between 65 and 200 mesh.

In the last stages of milling, water is added along with chemicals to condition the ore for froth flotation.

Flotation is a continuous process that uses compressed air and various flotation chemicals to separate the ore into fractions. By proper selection of additives, certain minerals are caused to float to the surface and are removed in a foam of air bubbles, while others sink and are carried out with the slurry. The ore passes through many flotation stages in order to accomplish this separation. The chemicals that are added are classified as "frothers", which create the foam; "collectors", which cause certain minerals to float; and "depressants", which cause certain minerals to sink.

In the flotation of copper ores, the frothers most often used are reportedly pine oils, cresylic acid, or long-chain alcohols (1). Lime is usually added in the final stages of grinding, both to adjust the pH of the slurry to an optimum level and to act as a depressant for iron pyrite. In this application it is often used in conjunction with cyanide (1). Various xanthates or dithiophosphates act as collectors for the valuable sulfide minerals, and the copper and other recoverable minerals come off with the froth (2). The gangue does not float and is discarded as "tailings".

After initial separation, the valuable minerals are sent through stages that further separate them by selective or differential flotation. By use of proper collectors or depressants, the concentrates may be upgraded to remove more iron pyrite. In some cases, other fractions high in lead and zinc, or molybdenum and rhenium, may be produced. These are usually sold to processors in the industries handling those metals. The copper ores of the west are a prime source for molybdenum; to separate this fraction, the concentrate must be steam stripped to remove the collector originally added (3).

Occasionally, a concentrator will batch-treat a copper concentrate with cyanide to dissolve its silver and gold content. After separating the leached solution from the concentrate, zinc metal is added to reprecipitate the precious metals.

Concentrates are dewatered by clarification and filtration. They may be partially dried to simplify handling and shipment, or may be more completely dried for direct "green" feed to a smelting furnace (see Process No. 5). Ten of the sixteen conventional smelters in this country have concentrator plants onsite or nearby (4).

Table 10 shows typical composition of copper concentrates; compositions vary with the character of the ore and the amount of processing employed.

2. Input Materials - Only sulfide ores of copper can be successfully separated by the flotation process. Oxidized ores are treated by hydrometallurgical processes (see Process No. 31).

Lime is used for pH adjustment and as a pyrite depressant. Quantities added vary between 0.9 and 18.0 kilograms per metric ton of ore processed (5). Pine oil frothers are usually consumed at a rate of about 0.09 kilogram per metric ton of ore (5). No data are available on the quantities of long-chain alcohols or cresylic acid required if they are substituted for pine oil.

Table 11 lists some of the chemicals that are used as collectors in the flotation process. The use and quantity of any one of these materials depends on the mineral assemblage particular to each ore type. Alkyl-based organic molecules are more commonly used than aryl compounds.

Miscellaneous compounds such as cyanides, zinc dust, various filter aids, and inorganic salts are occasionally used in small quantities.

3. Operating Conditions - Most portions of this process are carried out at ambient temperatures in closed buildings. At few points temperatures may approach 100°C (i.e., steam stripping for molybdenite concentration). Occasionally circulating streams are heated slightly to retain efficiency during cold weather.

4. Utilities - In 1973, usage of water at 21 copper concentrators ranged from about 100 to 500 cubic meters of water per metric ton of concentrate produced, the amount depending on the complexity of the process employed (4). In the same year, concentrators consumed about 6630 million kilowatt-hours of electricity, which is about 400 kilowatt-hours per metric ton of primary refined copper (2,6). The greater part of this electricity was used to operate the crushing and grinding equipment, with a smaller amount for production of compressed air.

5. Waste Streams - The handling and milling of dry ore is the principal source of air pollutants in this process. Items of equipment are always enclosed, but transitions between pieces of equipment are difficult to seal tightly. Ore classifiers are not always completely sealed. Dust quantity is reported as about 1 kilogram per metric ton of ore (3).

TABLE 10. ANALYSIS OF COPPER CONCENTRATE (7)

Element	Composition, % weight
Cu	20 - 50
S	30 - 38
Pb	tr. - 0.67
Fe	20 - 30
Zn	0.2 - 4.0
Ag	0.13
Au	31.5[a]
Pt etc.	tr.
Pd	tr.
As	tr. - 4.0
Sb	tr. - 0.36
Bi	tr. - 0.05
Se	tr. - 0.03
Te	tr.
Re	tr.
Ni	tr. - 0.1
Co	tr. - 0.02
Cd	tr. - 0.01
In	tr.
Ge	tr.
Sn	tr.
Cl	0.05
F	0.05
Al	Varies
Si	Varies
Ca	Varies
Mg	tr.
Mo	tr.
Mn	tr.
Flotation reagents	tr.

[a] Value for Au in grams/metric ton.

tr. = trace

TABLE 11. TYPICAL FLOTATION COLLECTORS (2)

Type	Formula[a]
Xanthate	ROCSSNa
Dithiophosphate	$(RO)_2PSSNa$
Dithiocarbamate	$R_2NCSSNa$
Thiol (mercaptan)	RSH
Thiocarbanilide	$(C_6H_5NH)_2CS$
Fatty acid soaps	RCOONa
Arenesulfonate or alkylarenesulfonate	RSO_3NA
Alkyl sulfate	$ROSO_3Na$
Primary amine	RNH_3Cl
Quaternary ammonium salt	$RN(CH_3)_3Cl$
Alkylpyridinium salt	$RC_5H_4N \cdot HCl$

[a] R is the abbreviation for an alkyl group such as $CH_3(CH_2)_n$. Although alkyl compounds are common, alkyl aryl compounds may also be used, as in alkylarenesulfonates.

This process produces the largest amount of wastewater in the industry. The ore flotation water is used to sluice the tailings into a pond, and suspended solids are the most critical pollutant in concentrator effluent (8). Although part of the water is recycled to the plant, the remainder is discarded. Excluding the amount lost by evaporation in the tailings pond, the volume of wastewater from this process will equal the water consumption, ranging from 100 to 500 cubic meters per metric ton of concentrate (3). In many cases in the Southwest, evaporation may equal consumption.

Reported analyses indicate that the water from the concentrator may contain up to 3500 milligrams per liter of dissolved solids, from 0.01 to 0.1 milligram per liter of cyanides, and ranges of metallic elements indicated in Table 12 (3).

The water may also contain thiosulfates and thionates, and the materials, both inorganic and organic, used as flotation additives.

More than 95 percent of all the ore brought from the mine is discharged from this process as tailings; this quantity totals approximately 241 million metric tons of waste material each year from the industry (2,6,9). Tailings are composed primarily of the common rock-forming minerals, but they also contain around 15 percent of the heavy metals originally found in the ore, and usually much of the iron pyrite. Production of higher-grade concentrates to minimize air pollution has increased the proportion of pyrites in the tailings. In this solid waste, the minerals have been pulverized and intimately mixed, and are therefore subject to weathering much more rapidly than rock masses of similar composition. They form a soil that is usually highly acidic and that contains no plant nutrients.

6. Control Technology - Dust from the milling operations is generally reduced by drawing air through the equipment and collecting the dust with cyclone separators. This is both a dust control and an integral part of the process since it allows these small particles to bypass one or more crushing and grinding operations. Fugitive dust is usually uncontrolled unless the amount being lost economically justifies the installation of equipment for its recovery. Dust control at the tailings pond may be accomplished through use of Coherex or a similar product.

Control of wastewater is discussed in more detail in following sections. This waste, although it is the major one, is rarely controlled independently, since waters from many sources find their way into the tailings pond. Occasionally this source is kept separate; the pond itself represents one stage of treatment.

Disposal of the tailings is a major problem in this industry. There is no universal solution for disposal of such vast quantities of solid materials; each concentrator plant requires separate study.

TABLE 12. METALLIC ELEMENTS IN CONCENTRATOR WASTEWATER (3)

Element	Concentration, mg/l
Arsenic	0.07 approximately
Antimony	0.2 to 1.0
Cadmium	0.02 to 0.05
Copper	0.08 to very high
Cobalt	0.04 to 1.68
Iron	0.1 to 2.0
Manganese	0.05 to 4.8
Mercury	0.001 to 0.05
Molybdenum	0.2 to 20
Nickel	0.05 to 3
Lead	0.01 to 3
Selenium	0.003 to 0.02
Silver	0.1 approximately
Strontium	0.03 to 2.5
Zinc	0.05 to 8.50

7. EPA Source Classification Code - None

8. References -

1. Hawley, John R. The Use, Characteristics and Toxicity of Mine-Mill Reagents in the Province of Ontario. Ontario Ministry of the Environment. Toronto, Ontario. 1977.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc., New York. 1967.

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4. Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry. Point Source Category Volumes I and II. EPA/1-75/032-6. U.S. Environmental Protection Agency, Washington, D.C. February 1975.

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8. Williams, Roy E. Waste Production and Disposal in Mining, Milling, and Metallurgical Industries. Miller Freeman Publications, Inc. San Francisco. 1975.

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Multiple-Hearth Roasting

1. Function - Roasting is frequently the first of the pyrometallurgical processes applied to the copper ore concentrate at the copper smelter. The purpose of roasting is to reduce the sulfur content so that subsequent processes operate efficiently. Roasting also removes the water from the concentrate, volatilizes some of the arsenic and antimony, and preheats the ore before it is charged as calcined feed to the reverberatory furnace.

Roasting is accomplished either with a multiple-hearth or fluidization process (See Process No. 4). In the multiple-hearth roaster, concentrate is introduced at the top of a cylindrical vessel fitted with a series of round horizontal trays, or hearths. The ore is raked across each hearth in turn until it is discharged from the bottom of the cylinder. Air is admitted into the roaster, along with a fuel if necessary to maintain adequately high temperature.

Most of the chemical reactions that occur in the roaster are with the pyrite in the concentrate rather than with the copper minerals. Copper has a higher affinity for sulfur, whereas iron combines preferentially with oxygen. Admitting a limited amount of air, therefore, causes the pyrite to oxidize, producing iron oxide and sulfur dioxide gas (1).

The heat of the roasting process generally vaporizes much of the arsenic and some of the antimony and other elements in the ore, and these "fumes" leave the roaster with the SO_2 gas.

Multiple-hearth roasting is currently in use at four domestic copper smelters. The roasters are built to handle from 125 to 650 metric tons of concentrate per day (2). There appears to be a trend away from their use except in "custom" smelters since with higher-grade concentrates the cost of operation frequently outweighs the benefits realized (1). Custom smelters may require multiple-hearth roasters, as the longer residence time and more moderate rate of temperature change may be advantageous in the separation of certain impurities, such as arsenic.

2. Input Materials - Copper concentrate, as received from the copper concentrator, is generally the only input. Composition is shown in Table 10 (Process No. 2). At some smelters, fluxes such as limestone and silica are placed on the lower hearths for premixing and preheating prior to the charging of the roasted calcine to the smelting furnace.

3. Operating Conditions - Multiple-hearth roasters generally operate at temperatures from 760°C on the bottom hearth down to around 200°C on the top hearth (3). The roaster operates under negative draft near atmospheric pressure.

4. Utilities - With the concentrates now being used, some fuel in the form of oil or natural gas is always required. If concentrates are especially high in sulfur content (24 percent or more), sufficient heat is released by the burning sulfur and supplemental fuel is required only to preheat the

roaster at startup (autogenous roasting). A reported energy requirement is 280,000 kilocalories per metric ton of copper produced (4).

Cooling air is circulated through a hollow shaft that drives the rake arms to prevent damage to mechanical bearings and seals.

Electricity is used to drive the roaster rakes and for auxiliary materials handling equipment. Approximately 5700 kilowatt-hours is required for a plant of 100,000 metric tons of copper per year capacity (5).

5. Waste Streams- Gases leaving most multiple-hearth roasters are too weak in SO_2 gas for direct use by a sulfuric acid plant unless the inlet air can be enriched in oxygen or unless air infiltration is reduced. The SO_2 concentration is variable, being dependent upon the required degree of sulfur removal and the amount of fuel necessary to maintain roasting temperatures. With lower-grade concentrates, 20 to 50 percent of the total SO_2 generated by smelter facilities once came from the roaster. Since fuel gas was not required, the emissions contained from 5 to 10 percent SO_2 (6). Published data on current operations are inconsistent and contradictory; recent reports give SO_2 concentrations in emissions from roasters at 0.5 to 2 percent (2,7,8,9,10,11,12). Gas from roasting is a steady stream, however, and if sufficiently concentrated in SO_2 is otherwise suitable for sulfuric acid manufacture.

Emissions of particulate matter from most multiple-hearth roasters are little affected by operational changes. About 75 kilograms of particulates are produced per metric ton of copper produced (5,9,10,11,13). Fifteen percent is present in sizes below 10 microns (14). Table 13 presents typical particle-size profiles. Although composition is dependent on the ore, particulates may be expected to contain the more volatile elements, such as arsenic, antimony, selenium, zinc, mercury, bismuth, rhenium, and lead. These will leave the roaster as vaporized materials. Some copper and iron will be physically carried over by the gas stream. Table 14 gives a weight analysis of particulate and fume emissions from a multiple-hearth roaster. Table 15 lists the typical levels of volatile metals found in copper ore concentrates. These metals apparently appear in these dusts as sulfates, sulfides, oxides, chlorides, and fluorides, but it is not known which of the metals is combined with each negative radical. There are significant fugitive emissions of dust and fume at some multiple-hearth roasters.

The multiple-hearth roaster produces no liquid wastes.

Any organic materials that enter the roaster with the copper concentrates are vaporized or decomposed in the roaster.

6. Control Technology - At present, none of the operating multiple-hearth roasters is equipped with controls for SO_2 emissions. The only suitable controls are the various scrubbing systems, as outlined for reverberatory furnace gases (Process No. 6).

TABLE 13. TYPICAL SIZE PROFILE OF MULTIPLE-HEARTH COPPER ROASTER EMISSIONS (15)

Size, microns	Percent by weight
Entrained particles, carried from the roaster as solids.	
230 - 218	4.6
149 - 230	4.0
100 - 149	5.3
74 - 100	7.4
44 - 74	10.6
28 - 44	12.8
20 - 28	6.8
10 - 20	8.0
< 10	10.5
Sublimed particles, condensed from metallic vapor.	
0.5 - 10	30.0

TABLE 14. CONCENTRATION AND WEIGHT ANALYSIS OF PARTICULATE EMISSIONS FROM A MULTIPLE-HEARTH COPPER ROASTER (15)

Concentration	Emission	
	Chemical	% Weight
Entrained particulates 1.4 g/Nm^3	Cu	23.8 - 34.5
	Fe	21.2 - 30.7
	S	1.7 - 2.5
	As	tr.
	Sb	tr.
	Pb	tr.
	Zn	tr.
	Sn	tr.
	Cd	tr.
	Ni	tr.
	Mn	tr.
	Se	tr.
	SiO_2, CaO $CaSO_4$	10 - 15
	O_2 (oxides)	13 - 19
	inerts	0.8
Sublimed particulates 0.6 g/Nm^3	As_2O_3	tr. - 17
	Sb_2O_3	tr. - 13
	inerts	tr.

TABLE 15. TYPICAL LEVELS OF VOLATILE METALS IN DOMESTIC COPPER ORE CONCENTRATES (6)

	Concentration level	Percent of concentrates surveyed
Lead	<5000 ppm	96
	5000 ppm-<2%	2
	≥2%	2
Zinc	<1%	67
	1-<4%	1
Arsenic	200-1000 ppm	88
	1000 ppm-1%	10
	>1%	2
Cadmium	<1000 ppm	100
Beryllium	<10 ppm	100
Vanadium	<100 ppm	100
Antimony	<200 ppm	97
	>200- 500 ppm	3
	>5000 ppm	1/2
Tin	<1000 ppm	100

The proposal has been made that enrichment of the air to a roaster with oxygen would increase its SO_2 content to a level where it could be used as feed to a sulfuric acid plant. This proposal has been rejected on several grounds by smelter operators. Most multiple-hearth roasters cannot mechanically withstand the high temperatures caused by oxygen enrichment. One company that recovers arsenic from flue dusts maintains that oxygen enrichment causes the arsenic to oxidize to As_2O_5 and prevents its removal by current techniques (16).

A variety of devices are used in various combinations for control of particulate emissions. Larger particulates are occasionally separated with cyclone collectors or with "balloon flues." The latter are oversized ducts in which flue gas velocity is reduced enough that the particles settle by gravity. Removal efficiency is 30 to 60 percent (16). Cyclones can remove 80 to 85 percent of the solids, but require an addition of energy to compensate for pressure drop. Smaller particles in the gas stream are separated by hot gas electrostatic precipitators, or the gas may be cooled with water sprays before entering an ESP unit or a baghouse. Control is not complete, especially in regard to sublimed particles and fugitive losses.

The collected dusts are returned to the metallurgical processing, usually to the smelting furnace. One smelter extracts arsenic trioxide before returning the dusts to the furnace. Excessive accumulation of impurities causes dusts to be discarded, but the means of disposal have not been reported.

7. EPA Source Classification Code - 3-03-005-02

8. References -

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Fluidization Roasting

1. Function - The function of fluidization roasting is the same as for multiple-hearth roasting (Process No. 3): to reduce the sulfur content of the concentrate and to oxidize some of the iron, so that the matte produced in the smelting process can be treated most efficiently in the copper converter. Roasting also volatilizes some impurities and preheats the reverberatory feed. The roasted concentrate to be smelted is called calcined feed.

The fluidization roaster is the pyrometallurgical application of the fluidized-bed principle that has revolutionized so many operations in other industries over the past 30 years. It is based on the discovery that particles of a solid added to a gas stream moving vertically upward at just the right velocity take on many of the characteristics of an agitated liquid. Each particle of the solid is in constant agitated motion, separated from all other particles, and is in intimate contact with the gas stream. Any chemical reaction that takes place between the solid and the gas happens very quickly, with no cold pockets or hot spots.

In the fluidization roaster, the gas is a recycled stream of flue gas, into which regulated streams of air and fuel gas are introduced. The solid is copper concentrate, continuously being fed and overflowing the fluidization vessel. Both the fuel and the oxygen are completely consumed; by elimination of excess air, the SO_2 content of the flue gas stream is greatly increased, to a concentration great enough for feed to a sulfuric acid plant.

If the sulfur content of the concentrate is high enough, fuel is needed only at startup. With 20 percent sulfur in the feed, sufficient heat is released by the sulfur to make additional fuel unnecessary. Operators of fluidization roasters, therefore, find it best not to process the ore into super-quality concentrates, but to tailor the quality of the concentrate to match the requirements of the roaster. Fluidization roasters may not provide sufficient residence time for volatilization of certain substances such as arsenopyrites (1).

Four domestic copper smelters have adopted fluidization roasting. Being complex and highly instrumented units, they must be capable of large throughput to justify the investment. Units with capacities from 700 to 1500 metric tons per day are in use (2).

2. Input Materials - Copper concentrate is the only input, usually blended or produced to a quality that the roaster can most economically process. The concentrate may be pelletized or granulated before being fed to the roaster.

3. Operating Conditions - Because of the thorough mixing in the fluid bed, temperature is held constant in all portions of the bed in the range of 650° to 760°C. The pressure in the bed is slightly above atmospheric, and in portions of the recycle stream the pressure may be 1 kilogram per square centimeter or more.

4. Utilities - The major utility used is electricity to compress the recycled gas, to inject air, and to operate auxiliary devices. No estimates of power consumption are published.

Fuel gas is the usual source of heat for starting the charge, although some plants have fuel oil facilities for standby. Quantity consumed is small.

Oxygen enrichment facilities are being considered for some of these units in order to provide more operating flexibility.

5. Waste Streams - Fluidization roasters are always fitted with cyclone separators that catch the large amounts of dust that rise from the bed. The dust is returned to the bed. Dust quantities can be as much as 75 percent of the feed (2,3). The cyclones are most properly considered as part of the process, and the waste stream considered the outlet of the cyclones. This waste stream contains particulates and fumes of the same chemical character as those from a multiple-hearth roaster (Process No. 3); they are rich in volatile elements such as arsenic and contain considerable copper. Data on total quantities of dust are not available; they are likely to be greater than emissions from a multiple-hearth roaster because of the more complete separation of smaller particles from the body of the charge.

Sulfur dioxide concentrations in the gas from the fluidization roaster are reported to be from 12 to 16 percent (2,4,5).

The roasting operation produces no liquid or solid wastes.

6. Control Technology - All the smelters that operate fluidization roasters use the SO_2 for production of sulfuric acid. Except for other processing to recover liquid SO_2 or elemental sulfur, this is the only known technology with which to dispose of such a concentrated gas stream.

Almost complete removal of particulates is required before the gas is introduced into a sulfur recovery process. Electrostatic precipitators and wet scrubbers are in use with the operating fluidization roasters. Since the dusts and condensed fumes contain valuable materials, they are normally returned to the pyrometallurgical processing units, usually to the smelting furnace, but some may be discarded.

7. EPA Source Classification Code - 3-03-005-02

8. References -

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Drying

1. Function - Copper concentrates that are not to be processed by roasting must pass through a dryer, whose only function is to decrease the moisture content. Drying may be practiced to simplify handling of the concentrate. In recent years it has been practiced to make the concentrate suitable for direct feed to the reverberatory furnace; this is described in the industry as "green feed." Excessive moisture in the concentrate may cause minor eruptions or explosions that may damage the furnace (1).

Some smelters continue to use existing multiple-hearth roasters, operated at much lower temperatures, to accomplish this drying operation. Special dryers, such as rotary kilns, are also being used. The dryer may be more conveniently located at the concentrator rather than at the smelter (see Process No. 2).

2. Input Materials - The concentrate containing 5 to 25 percent moisture is the only input. Analysis is given in Table 10.

3. Operating Conditions - Except at flame fronts, temperatures in the drying operation do not exceed 150°C. Pressures are atmospheric.

4. Utilities - Fuel gas is most frequently used for concentrate drying, although facilities for substitution of oil are usually provided. One report calculates that for a plant yielding 91,000 metric tons of refined copper per year, the drying heat from fossil fuels would be equivalent to 17,200 kilocalories per hour of dryer operation (2).

Electricity is used for conveyors and mechanical operation of a dryer. The report cited above estimates 2700 kilowatt-hours for the same size plant (2).

5. Waste Streams - Dust generated by a drying operation would be of the same composition as the input concentrate. A foreign plant using a multiple-hearth roaster for drying reports particulate emissions of 0.05 percent of the weight of the feed. No data for domestic plants have been reported.

Small quantities of organic materials in the concentrate could be decomposed or volatilized in the drying operation, but no data have been reported. Emissions of metallic fumes or oxides of sulfur are unlikely.

6. Control Technology - Dust from a drying operation frequently consists of the fine particles present in the ore, and their collection is complicated by the ready condensation of moisture in the warm effluent. If a dryer is installed at a concentrator plant, the best control is to remove the dust by wet scrubbing and return it to the final stages of the flotation process. If a multiple-hearth roaster is used for drying, balloon flues or other particulate removal equipment may be modified to handle this wet dust. Bag filters generally produce a caked product that must be redried; they are effective, although troublesome, collectors (3,4).

Quantities of the organic materials in the concentrate are believed to be small enough that these materials require no separate treatment.

7. EPA Source Classification Code - 3-03-005-06

8. References -

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4. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. Arthur G. McKee & Co. for U.S. DHEW. June 1969.

Reverberatory Smelting

1. Function - Copper smelting is the process of removing from a roasted or dried ore concentrate much of its iron and some undesirable impurities, leaving a molten mixture that can be processed efficiently by a copper converter. This is most often accomplished with a reverberatory furnace. It may, however, be accomplished by other methods (see Process No's. 7, 8, and 11).

Reverberatory smelting, the oldest of the copper smelting processes now in use, is little different now than when it was first practiced in 1879. It is in use at 11 of the 16 smelters in this country, in one or two modifications, described as either "deep bath" or "dry hearth." Some reverberatory furnaces are very large, capable of accepting as much as 1800 metric tons of material per charge (1).

The reverberatory furnace is a large, arch-roofed, horizontal chamber into which ore concentrate and flux are charged. The term "reverberatory" refers to the configuration of the flame which enters the chamber from one end, reverberates off the roof and strikes the charge from above. As the temperature of the charge increases, a complex series of reactions takes place and the charge separates into fractions. One fraction is a gas, consisting of SO_2 and volatiles, which mix into the combustion off-gases. Two other fractions are molten liquids, the copper matte and slag, which are not soluble in each other and therefore separate into layers.

The matte layer consists primarily of copper and iron sulfides and small quantities of molten copper metal, which are mutually soluble. Since copper has a weak chemical affinity for oxygen, very little copper oxide is formed and almost all of the copper in the charge accumulates in the matte layer. Iron, on the other hand, combines readily with oxygen to form iron oxides, which in turn react with silica flux to form iron silicates. These compounds, plus the calcium, magnesium, and aluminum minerals that were present in the concentrate, form a lighter-density slag that floats on top of the matte. Any sulfur in the charge that is left over from the slag- and matte-forming reactions reacts with additional oxygen to form SO_2 gas.

The charge to the reverberatory furnace is proportioned so that the resulting matte typically contains 40 to 45 percent copper and 25 to 30 percent each of iron and sulfur (2). The matte contains most of the heavy elements present in the charge, practically all the gold and silver, and part of the arsenic and antimony. Some of the arsenic, selenium, and other trace elements form volatile compounds and are carried away in the gas stream.

Slag is drained periodically from a skimming bay at one end of the reverberatory furnace. Matte is also withdrawn periodically through tap holes in the lower furnace wall. Off-gas from the furnace is usually sent through waste heat boilers to recover a portion of the excess energy.

2. Input Materials - The primary input material is the roasted or dried concentrate, not much different from the concentrate received from the mill. Slags from the converter and anode furnace are added for reprocessing, as are flue dusts from dust collection equipment throughout the smelter. Precipitates from hydrometallurgical operations or materials from refinery processing may be added at this step. At some smelters, impure scrap copper is reprocessed as part of the change.

Flux normally consists of sand high in silica content, and usually limestone to make the slag more fluid. Sometimes "direct smelting ore" is used, which adds both fluxing material and additional copper.

Composition of one charge to a reverberatory furnace in Arizona is reported as follows in Table 16.

TABLE 16. COMPOSITION OF CHARGE TO A REVERBERATORY FURNACE (1)

Ore concentrate	65%
Converter slag	25%
Hydrometallurgical precipitate	2%
Flue dusts	1%
Silica flux	1%
Limestone flux	6%

This charge produced molten materials of which 47 percent was matte and 53 percent was slag.

3. Operating Conditions - When possible, the concentrate is charged into the furnace while still hot from the roaster (400°C or more). Converter slag is charged as a liquid (1100°C approximately). Other materials are usually charged at ambient temperatures. The reverberatory furnace usually heats the mixed charge to at least 1000°C before the matte forms and separates; temperatures up to 1300°C have been reported (3). All operations are at or near atmospheric pressure.

4. Utilities - It is estimated that 90 percent of the energy requirements for a smelting operation is consumed in the reverberatory furnace (4). It is reported that 18 billion kilowatt-hours of energy was used in domestic copper smelters in 1973 (4). Consumption of energy by this process is very high; it is usually supplied in the form of natural gas, but pulverized coal or fuel oil can be used. It is estimated that 500,000 kilocalories of heat is required to smelt 1 metric ton of concentrate if the charge is preheated by a roasting operation. If the charge is not preheated, an additional 390,000 kilocalories is required (5). These values give credit for steam generated by waste heat boilers, which are almost always installed with a reverberatory furnace. The reverberatory furnace is in itself thermally inefficient, using more than 4 times the heat theoretically required (6).

Noncontact cooling water is used by copper smelters primarily for the protection of equipment auxiliary to the roaster, converter, and reverberatory furnace. Data that allocate this cooling load specifically to each process are not available. Reported data indicate that the total cooling water consumption for smelting operations can vary from 4000 to 61,000 liters per metric ton of copper product.

Contact cooling water is used at four smelters to granulate the slag from the reverberatory furnace. One smelter uses 1.7 million liters of water per day for this purpose (2).

5. Waste Streams - It is reported that 20 to 45 percent of the sulfur that enters with the ore concentrate is emitted by the reverberatory furnace as SO_2 (3,7,8). Although most smelter operators have attempted to make operational changes to reduce this quantity, no recent data are available. The gas is released as a dilute stream of variable composition, reported as being from 0.5 to 2.5 weight percent SO_2 (3,8,9,10,11,12). Other constituents in the exit gas are shown in Table 18, for unroasted and roasted concentrate feeds. The volume of this gas is very large since it consists primarily of the combustion gases from the heating fuels. Temperature of the exit gases may reach 1150° to 1200°C (10).

Between 14 and 40 kilograms of particulate matter is emitted in this gas stream per metric ton of copper matte produced (8,11,13,14). One analysis of the particulates showed 24 percent copper and concentrations of other elements as shown in Table 17.

TABLE 17. ANALYSIS OF PARTICULATES EMITTED FROM A REVERBERATORY FURNACE (15)

	mg/l
Zinc	44,000
Cadmium	310
Manganese	100
Chromium	45
Nickel	35
Mercury	2.5

Other investigations indicate that most of the volatilized arsenic, selenium, lead, antimony, cadmium, chromium, and zinc emissions will be generated in the reverberatory furnace (10,11,14,16,17,18).

Fugitive dust is generated in this process as materials are loaded into the furnace, but no quantities have been reported.

The only liquid waste from this process is the run-off from slag granulation. Three complete analyses are shown in Table 19. Liquid waste is most often generated as the overflow from a pond into which the molten slag is dumped. Since the pond is an open body of usually hot water, subject to rainfall and evaporation, quantity and composition of the overflow may be highly variable.

One copper smelter is situated close to a market for the furnace slag it produces; for all the others, slag constitutes a large quantity of solid

TABLE 18. COMPOSITION OF REVERBERATORY FURNACE EXHAUST GASES (12)

Component	Green feed, % weight	Calcined feed, % weight
Carbon dioxide	8.4	10.2
Nitrogen	69.3	71.0
Oxygen	0.25 - 1.0	0.25 - 1.0
Water	18.8	17.7
Sulfur dioxide	1.5 - 2.5	0.6

TABLE 19. EFFLUENTS FROM SLAG GRANULATION (16)
(mg/l)

Parameter	Plant 103	Plant 110	Plant 102
pH	7.7	8.1	6.4-7.6
TDS	140.	3800.	
TSS	6.8	151.	
$SO_4^=$	62.	310.	
CN-	0.005	0.050	0.030
As	3.7	0.048	5.70
Cd	0.001	0.001	0.042
Cu	0.12	0.05	0.604
Fe	0.04	0.03	340.
Pb	0.04	0.070	7.4
Hg	0.0001	0.0001	0.0001
Ni	0.001	0.06	0.16
Se	0.001	0.54	0.040
Te	0.001		0.100
Zn	0.44	0.023	36.
Oil and grease		0.0	0.02

waste, as much as 3000 kilograms per metric ton of copper produced (15). Table 20 gives an analysis of trace elements found in a reverberatory furnace slag. The bulk of the slag is a mixture of iron silicates, as shown also in Table 20.

6. Control Technology - Gases from the reverberatory furnace pass through a waste heat boiler and then through an electrostatic precipitator for particulate removal. The gases may pass through spray collectors or balloon flues before entering the ESP units. The degree of particulate removal ranges from 50 to 99.9 percent. Particulates collected are recycled into the metallurgical process, normally as part of the reverberatory furnace charge, but accumulation of trace elements causes some flue dusts to be discharged or processed separately. Quantities and their disposition are not reported.

At present, there is virtually no demonstrated economic method for control of the SO_2 emissions from reverberatory smelters. One smelter constructed a plant to absorb the SO_2 from this stream in dimethylaniline and regenerate it as a concentrated stream for further processing, but it is not now operating. One Canadian smelter uses an ammonia absorption process on some smelter streams, but this system is not in use domestically. Other scrubbing solutions, containing compounds of zinc and aluminum, are used on smelter gases in Japan. Scrubbers using lime or limestone, with and without magnesium addition, are being used on sulfur-containing flue gases from coal-fired boilers in the United States, and might be adopted for use in U.S. smelters, as has been done in Japan. Another absorption process based on sodium sulfite-bisulfite is being tested.

An alternate method of controlling SO_2 emissions is to increase the concentration of the off-gas to a level sufficient for sulfuric acid production. Such a strategy has been successfully implemented in a number of Japanese furnaces of conventional design and operation. Methods include fuel-rich or oxygen-enriched combustion, use of preheated secondary air in order to achieve rapid smelting and sulfur release, use of high grade concentrates, instrument controlled combustion and feeding for steady level of operation, or simply tighter construction and leak control. One Japanese smelter achieves high SO_2 concentrations by blending the reverberatory off-gas with the exhaust from a continuous furnace that combines the functions of roasting, smelting, and converting. At another Japanese smelter, the reverberatory exhaust is blended with the convertor off-gas and scrubbed with a magnesium hydroxide slurry, forming magnesium sulfite, which can be decomposed by calcination to MgO and concentrated SO_2 (19).

Of the four smelters that practice slag granulation, one reports no wastewater from this source since the rate of evaporation at this location necessitates a continuous water make-up to the quenching pond. The other three smelters mix the water from slag granulation with other wastes (2,20).

TABLE 20. GENERAL RANGE OF REVERBERATORY FURNACE SLAG COMPOSITION

Compound or element	Composition, percent weight
FeO	34 to 40
SiO_2	35 to 40
CaO	3 to 7
MgO	0.5 to 3
Al_2O_3	4.5 to 10
Copper	0.4 to 0.7
Sulfur	1.0 to 1.5

Trace elements	Parts per million
Zinc	Approximately 7800
Magnanese	Approximately 450
Antimony	Approximately 400
Lead	Approximately 100
Chromium	Approximately 100
Selenium	Approximately 20
Nickel	Approximately 25
Cadmium	Approximately 10
Mercury	Less than 1.0
Arsenic	Trace
Tellurium	Trace
Cobalt	Trace

Granulated slag is usually a coarse-grained material of low to medium density, usually discarded near the smelter. A small amount may find a market for use as road fill or concrete aggregate. Crushed slag that has not been granulated also finds a small market for these same purposes. Most slag is not granulated, but is simply poured out and allowed to solidify. There is no easy way to reclaim the slag dumping areas, and there are no published reports on how this could be done. It is generally assumed that the potential of secondary water pollution from slag dumps is less than that from mine spoil or tailings beds.

7. EPA Source Classification Code - 3-03-005-03

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17. Davis, W.E. National Inventory of Sources and Emissions: Copper, Selenium, and Zinc. PB-210 679, PB-210 678, and PB-210 677. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. May 1972.

18. Phillips, A.J. The World's Most Complex Metallurgy (Copper, Lead, and Zinc). Transactions of the Metallurgical Society of AIME. Volume 224: pp. 657-668. August 1962.

19. SO_2 Control for the Primary Copper Smelter Reverberatory Furnace, Pacific Environmental Services, Inc. EPA Draft Report. April 1977.

20. Assessment of the Adequacy of Pollution Control Technology for Energy Conserving Manufacturing Process Options. Industry Assessment Report on the Primary Copper Industry. Arthur D. Little, Inc. Draft. October 1974.

Electric Smelting

1. Function - Copper smelting is the process of removing from an ore concentrate a portion of its iron and sulfur content in order to produce a molten mixture that can be treated efficiently in subsequent processing. Smelting requires only the application of heat to produce matte and slag from a charge of minerals. Three other smelting methods are used (Process No's. 6, 8, and 11). In electric furnace smelting, heat is supplied by electricity.

Electric furnaces for copper smelting are similar to those used in other metallurgical industries. Three electric furnace installations in the United States are used for copper smelting. Capacities are up to 1350 metric tons of total charge per day.

2. Input Materials - The principal input is copper ore concentrates processed or blended to a suitable composition. Various fluxing materials are also required. The charge materials are similar to those outlined for a reverberatory furnace (Process No. 6).

Electric smelting requires the use of carbon electrodes to conduct electric current into the layer of slag. Various types of carbon electrodes can be used. These electrodes are consumed during operation. In one U.S. smelter, a proprietary paste carbon mixture is consumed at a rate of 2.5 kilograms per metric ton of charge (1).

3. Operating Conditions - The charge is usually heated to temperatures between 1000° and 1300°C, and the electric furnace is operated at a small negative pressure (2). Electric furnaces are normally enclosed in a large building.

4. Utilities - When hot concentrate is fed from a roasting process, electric energy is consumed at a rate of 605 kilowatt-hours per metric ton of total feed (1). Use of cold feed requires 990 kilowatt-hours per metric ton of concentrate (3). No direct combustion of fuel takes place in electric smelting.

The furnace must be cooled to protect some of the components from high temperatures. Cooling is done partially by infiltration of air into the furnace, but some external cooling is also required. Either water or air can be used, the quantity depending on furnace design. Infiltration of air is also required to ensure complete oxidation of liberated sulfur. Operators of one electric smelter report that 110 cubic meters per minute of air is circulated each second to cool a furnace of 51,000 KVA transformer capacity (4).

5. Waste Streams - SO_2 in the gas emitted from an electric furnace is more highly concentrated and temperatures are lower than in emissions from a reverberatory furnace. SO_2 concentration can range from 3 to 8 percent (3). Within limits this can be adjusted to make the gas suitable for sulfuric acid production. The electric furnace may produce small amounts of hydrogen gas and carbon monoxide, but sufficient air infiltrates to oxidize these combus-

tible materials. Very small amounts of hydrocarbons released from the electrode compounds will also burn.

Because of the lower gas volumes and more uniform gas flow, emissions of particulate matter would be expected to be lower than with a reverberatory furnace; no published estimates are available. Particulate composition would be about the same as from a reverberatory furnace (Process No. 6).

Slags and wastewaters from slag granulation would be similar to those of the reverberatory furnace, although more complete removal of copper and sulfur compounds from electric furnace slags is likely.

6. Control Technology - The three operating electric smelters in this country use the gases from the furnaces for sulfuric acid manufacture. In each case the gas stream is first combined with that from another furnace, such as a fluidized roaster or converter. Acid manufacture is the best available technology for SO_2 removal from electric furnaces, since the sulfur content is high enough for that application.

Control of the slag as a solid waste, or lack of controls, is described in reference to the reverberatory furnace (Process No. 6).

The small waste water stream from slag granulation is invariably mixed with other streams for treatment.

7. EPA Source Classification Code - 3-03-005-03

8. References -

1. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency, Washington, D.C. September 1973.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc., New York. 1967.

3. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

4. Cole, R.C. Inspiration's Copper Smelter Facilities. Mining Congress Journal. October 1973. p. 22-32.

Flash Smelting

1. Function - Copper smelting is the process of removing from an ore concentrate a portion of its iron and sulfur content in order to produce a molten mixture that can be treated efficiently by a copper converter. Until about 25 years ago, only two batch-type smelting processes were available, both inefficient in energy consumption (see Process No's. 6 and 7). Since that time, a continuous flash smelting process has been developed. This process performs the smelting function at a much higher thermal efficiency while producing a continuous, more easily controlled stream of flue gas, with a high SO_2 content (1).

In flash smelting, ore concentrates are injected along with flux and preheated air into a combustion chamber. Part of the sulfur of the concentrate burns in a "flash" combustion while the particles are falling through the chamber. The heat from this combustion maintains smelting temperature. Matte and slag form in the chamber and separate into layers as in a reverberatory furnace. The matte is sent to a conventional converter for further processing, and the slag, which contains too much copper to discard, is also further processed (see Process No. 12).

One smelter in the United States is operating an Outokumpu flash smelting unit that was developed in Finland. This version is in extensive use in several other countries. Another flash smelter design (INCO), using pure oxygen, is operating in Canada.

2. Input Materials - Copper concentrates especially tailored for flash smelting are the primary input. Not all concentrates are suitable for this process. The concentrates must be finely pulverized (50 percent minus 200 mesh) (2), and must contain very low concentrations of lead, zinc, and other volatile metals. They must have a fairly high sulfur-to-copper ratio, and thus are not high-grade concentrates. The concentrates are not preroasted, unless they contain considerable arsenic, but must be dried. Precipitates from hydrometallurgical operations cannot normally be handled by a flash smelter.

Flux in the form of silica sand or crushed rock must be prepared in a separate milling process to 80 percent through 14 mesh (2) and must also be dried. High grade "direct smelting" concentrates can be substituted if available.

3. Operating Conditions - Temperature in the flash chamber is maintained at approximately 1100°C (1). Pressure is approximately atmospheric.

4. Utilities - Fuel consumption in the Outokumpu flash smelter is only about two-thirds of that required by a reverberatory furnace in equivalent production (2,3). Except for startup or abnormal operations, fuel is required only to preheat the combustion air. This is reported as 7,560,000 kilocalories per hour for copper production of 100,000 metric tons per year (2). Any fossil fuel can be used.

Natural gas or oil is used to heat the furnace to startup temperature. Oil can also be used, if required, to maintain smelting temperatures with some concentrates.

Electrical power is used to operate feed and air injection equipment as well as the complex instrumentation this process requires. An estimate of 600 kilowatt-hours for a 91,000 metric ton per year copper plant has been reported (4).

5. Waste Streams - Flash smelting removes a large percentage of the sulfur from the concentrate. From 50 to 80 percent is converted to SO_2, which leaves as a stream of 10 to 20 percent concentration. In Finland the concentrates are blended to produce a 14 percent SO_2 concentration, which is ideal for a suitably-designed sulfuric acid plant (5).

Particulates in the gas stream are expected to equal about 6 to 7 percent of the feed, which is about the same as in the reverberatory furnace. Composition should be about the same as that of effluent from a reverberatory furnace, except that content of volatile metals should be lower since they are lower in the feedstock. Care is taken to keep zinc and lead to a minimum in the concentrates, since they tend to plate out within the flash chamber.

There are no solid or liquid wastes from flash smelting. The slag is discharged to waste from the electric furnace slag treatment process (Process No. 12).

6. Control Technology - An important objective in development of the flash smelting process was sale of the sulfur. There was a good market for sulfuric acid near the Finnish smelter (5); continuous and stable production of SO_2 made acid production most efficient. Flash smelting therefore was not developed with production of copper as the sole consideration.

It is possible, for reasons of energy economy, that flash smelters will be built in this country where there is no local market for sulfur compounds. The best currently available technology for control of SO_2 emissions would still be sulfuric acid production, even if the acid were then neutralized and discarded. Wet scrubbing would be an expensive, although satisfactory, alternative. The flash smelter in this country uses the gas for acid manufacture.

Complete removal of particulates is required for sulfuric acid manufacture, and recovered dusts would be blended back into the flash smelter feed. Cyclones, balloon flues, electrostatic precipitators, and wet scrubbers afford satisfactory methods for removal.

7. EPA Source Classification Code - 3-03-005-03

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc., New York. 1967.
2. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.
3. Metallurgy Processing in 1974. Mining Congress Journal, February 1975.
4. Personnal Communication with Mr. Paterson. Elken - Spigerverket a/s, New York, New York.
5. Treilhard, D.G. Copper-State of the Art. Engineering/Mining Journal. April 1973.

Peirce-Smith Converting

1. Function - A copper converter produces crude blister copper metal from the matte that is formed in the smelting process. The Peirce-Smith converter is the type most often used by copper producers in this country. See also Process No. 10 for an alternate converting method.

Matte is a molten mixture containing copper, iron, and sulfur. In the converter, a flux is added to the matte and compressed air is blown into the mixture through a series of openings called tuyeres. The remaining sulfur is oxidized to SO_2 and leaves with the flue gases. The iron forms into a slag that is returned to the smelting process. The blister copper is removed for further processing.

2. Input Materials - Matte from the smelting process is the principal input. Scrap copper being recycled is also introduced at this step, as is scrap produced within the smelter from spills or ladle "skulls," and materials from other processes with high concentrations of metallic copper. Flux used in the converter is sand or crushed rock with a high silica content. Sulfur is added if necessary to maintain the proper ratio of copper to sulfur.

Table 21 shows an average charge and product distribution from one copper converter.

3. Operating Conditions - To ensure that a slag of proper composition is formed and separated from the molten copper, converter temperatures are carefully controlled at 1175° to 1200°C (1,2). The converter operates at atmospheric pressure.

4. Utilities - The converting process itself consumes no fuel, since oxidation of the remaining sulfur furnishes enough heat to keep the mixture at the proper temperature. Any excess heat is removed by addition of cold copper scrap. The proper quantity of sulfur is obtained by carefully controlling the previous smelting operation. However, considerable quantities of fuel are required to reheat a cold converter, especially if it has been retired from the campaign for repairs.

Electricity is used to rotate the converter to discharge the slag and product.

Compressed air is required for oxidation of sulfur and iron. No data are reported on the required quantities.

A small amount of cooling water is used for noncontact cooling of some of the converter sections and auxiliaries.

5. Waste Streams - The converter emits about 120 kilograms of particulate matte per metric ton of copper produced (3,4,5,6). Tables 22 and 23 provide data on converter dust from some Arizona smelters, and Table 24 gives an analysis of particulates from a smelter in Nevada.

TABLE 21. MATERIAL BALANCE ON CONVERTERS - SMELTER IN ARIZONA (1)
percent, weight

Material	Input	Output
Reverberatory matte	78	
Silica	13	
Scrap and brass, etc.	4	
Reverts	4	
Sulfur	0.5	
Blister copper		28
Slag		67
Sulfur Dioxide		2
Flue dust		3

TABLE 22. COMPOSITION OF CONVERTER DUST (7)

Component	Percent, weight
Cu	10 - 19.0
Fe	10 - 20.0
Pb	0.83 - 2.5
Bi	0.61
F	nil
Sb	nil
As	0.04 - 0.6
Se	0.03 - 0.5
Si	5.0 - 15.0
Mg	0.57
Mo	0.08
Al	0.4 - 3.60
O_2	21.0
Cl	nil
Te	0.005 - 0.01
S	12.0
Ca	1.0

TABLE 23. PARTICLE SIZE DISTRIBUTION IN CONVERTER DUST (7)

Mesh	Percent, weight
-48 to + 65	0.5
-65 to + 100	1.5
-100 to + 150	2.5
-150 to + 200	3.5
-200 to + 270	5.0
-270 to + 325	5.0
-325 to + 32 microns	16.6
-32 microns to + 25 microns	55.6
-25 microns	9.8

TABLE 24. PARTICULATE EMISSIONS ANALYSIS AT STACK OUTLET FOR REVERBERATORY FURNACE AND CONVERTER[a]

Metal	Percent, weight
Arsenic	0.038
Cadmium	0.008
Copper	5.6
Selenium	0.014
Zinc	1.1
Chromium	0.006
Manganese	0.023
Nickel	0.0045
Vanadium	0.0023
Boron	0.12
Barium	0.03
Mercury	0.0007
Lead	0.065
Total	7.0115

[a] Stack test data (5/13/71).

Peirce-Smith converters are designed to be partially covered by a hood that catches the SO_2 and particulate emissions from the converter, but also draws in a considerable amount of uncontaminated air. By stoichiometric calculations, the SO_2 content in converter gases varies from 15 to 20 percent at various stages in the processing of a charge, but when diluted by the excess air the resulting mixture contains from 4 to 10 percent SO_2 (2,4,5,7,8,9). Some converters may produce gas with SO_2 content as low as 2 percent (5,7). Because the mouth of the Peirce-Smith converter is rotated from under the hood when flux is added and when slag and copper are poured out, local losses of SO_2, particulate, and fume occur during those periods.

Table 25 gives the composition of converter off-gas from an Arizona smelter.

Fugitive dust and fumes are generated in considerable quantities in a converting operation. Measurement of the quantities has not been possible to date.

There are no solid or liquid wastes from the converter process.

6. Control Technology - Gases from a Peirce-Smith converter are sometimes combined with the gas stream from a smelting or roasting process for particle removal and further treatment. The converter SO_2 stream is usually controlled through sulfuric acid plants.

Technology for control of a mixed gas stream including converter off-gas is discussed with the various smelting and roasting processes (Process No's. 3, 4, 6, 7, and 8).

7. EPA Source Classification Code - 3-03-005-04

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc., New York. 1967.

2. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

3. Vandegrift, A.E., L.J. Shannon, P.G. Gorman, E.W. Lawless, E.E. Sallee, and M. Reichel. Particulate Pollutant System Study - Mass Emissions, Volumes 1, 2 and 3. PB-203 128, PB-203 522, and PB-203 521. U.S. Environmental Protection Agency, Durham, North Carolina. May 1971.

4. High, M.D. and M.E. Lukey. Exhaust Gases from Combustion and Industrial Processes. PB-204 861. U.S. Environmental Protection Agency, Durham, North Carolina. October 1971.

TABLE 25. CONVERTER OFF-GAS COMPOSITION (7,11)

Component	Percent by volume
N_2	80
O_2	11
SO_2	6.9 - 9.8
SO_3	0.05 - 0.07
Dust	0.0053 g/lit max.

5. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation, Park Ridge, New Jersey. 1972.

6. Statnick, R.M. Measurement of Sulfur Dioxide, Particulate and Trace Elements in Copper Smelter, Converter and Roaster/Reverberatory Gas Streams. PB-238 095. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

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8. Control of Sulfur Oxide Emissions in Copper, Lead, and Zinc Smelting. Bureau of Mines Information Circular 8527, 1971.

9. Halley, J.H. and B.E. McNay. Current Smelting Systems and Their Relation to Air Pollution. Arthur G. McKee and Company, San Francisco, California 35224. September 1970.

10. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. Arthur G. McKee & Co. for U.S. Department of HE&W. June 1969.

Hoboken Converting

1. Function - The Hoboken converter is one type of furnace used to produce crude blister copper from the matte formed in the smelting process. Its function is identical to that of the Peirce-Smith converter (Process No. 9). The principal difference is that the flue that removes the gas from the converter is an integral part of the converter construction instead of being a hood mounted above it. This design minimizes infiltration of uncontaminated air, should minimize local losses of SO_2 from the converter mouth, and allows production of a gas with a higher and more uniform SO_2 content.

One smelter in this country uses Hoboken converters; however, optimal operation has not been achieved. They are used at several smelters in Europe and South America. The potential operating advantages of this design have not been clearly documented, and there have been no test programs to characterize the level of fugitive emissions.

2. Input Materials - These are the same as for Peirce-Smith converters, consisting largely of matte from the smelters, plus silica flux and cold copper scrap.

3. Operating Conditions - These are also the same as for a Peirce-Smith unit, 1200°C at atmospheric pressure.

4. Utilities - These are also the same as for Peirce-Smith. No supplemental fuel is required for the converting process.

5. Waste Streams - Since particulate matter is generated by the air being blown through the converter charge, particulate emissions should be comparable to those of the Peirce-Smith.

The SO_2 content of the gas stream from this converter could be at least 8 percent if three or more converters are operating, and may reach as high as 13 percent. It is calculated that with oxygen enrichment, the SO_2 concentration could be increased to 10 to 14 percent (1,2).

There are no solid or liquid wastes.

6. Control Technology - Production of SO_2 by the Hoboken converter is intermittent, but a battery of several of the converters will produce a stream sufficiently constant in rate to allow the gas to be used for sulfuric acid manufacture. This has been demonstrated by a smelter in Poland in which this is the normal operating procedure. The one domestic smelter using Hoboken equipment mixes the gas stream with the emissions from an electric smelter, and after particulate removal, uses the combined stream for sulfuric acid manufacture. At the Polish smelter separate fans remove the gases from each converter, and fugitive emissions are minimized by increasing the draft to each converter and creating negative pressure during such operations as charging and pouring. At the U.S. smelter with Hobokens, the converter exhausts are connected in parallel and such individual control is not possible.

7. EPA Source Classification Code - 3-03-005-04

8. References -

1. Cole, R.C. Inspiration's Copper Smelter Facilities. Mining Congress Journal. October 1974. pp. 22-32.

2. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

Noranda

1. Function - Noranda is one design of a continuous smelter, which in a single furnace combines most of the functions of roasting, smelting, and converting. This process approaches a one-step method of producing copper metal from ore concentrates. A Noranda installation is operating in Utah. One other unit is operated by the developer in Canada.

The Noranda furnace is a horizontal cylinder about 21 meters long, into which a mixture of concentrate and flux is continuously fed, along with fuel and oxygen. The furnace is fired from both end walls. The mixture reacts to form copper, matte, and slag, which separate into layers as in the batch smelting processes. Additional oxygen-enriched air is blown through 63 side-mounted tuyeres into the matte layer, forming blister copper, which collects in a third liquid layer below the matte. Slag and copper matte are intermittently tapped from the furnace. Noranda slag contains 3 to 8 percent copper, and is processed to recover the copper content (see Process No. 13).

Noranda does not completely eliminate the use of the copper converter. Blister copper from Noranda contains from 1.5 to 2.0 percent sulfur, and is usually batch treated in a standard converter to remove additional sulfur prior to fire refining. If the concentrate contains considerable impurity elements, the developer recommends that Noranda be used as a smelter only, to produce a high-grade matte for separate conversion to blister copper (1,2,3). This is the mode of operation at the one U.S. facility (4).

2. Input Materials - As operated at the U.S. installation, the charge consists of smelter reverts, and a pelletized mix of copper concentrate, reactor slag concentrate, copper precipitators, and flux.

3. Operating Conditions - This process operates at approximately atmospheric pressure. Temperatures in the U.S. installation are higher than 1200°C, which is the slag temperature (4).

4. Utilities - A principal advantage of Noranda is its efficient utilization of fuel. Heat losses during transfer of concentrate from the roaster to the reverberatory furnace are suppressed, as well as heat losses during the transfer of the matte from the reverberatory furnace to the converter. In addition, the net heat of oxidation is used for smelting. Fuel is only required to augment the fuel value of the sulfur and iron in the concentrate. With oxygen enrichment, about 440,000 kilocalories of heat is required to produce a metric ton of copper, which is about 22 percent of that required by a reverberatory furnace. The domestic Noranda reactor uses a gas-oil burner at one end and an oxygen-fuel burner at the other (1,2,3,4).

The fuel consumption reported above was based upon enrichment of combustion air to 50 percent oxygen, and of tuyere air to 35 percent. Although oxygen enrichment is not necessary with the Noranda process, best economy requires its use.

Small amounts of electricity are used for feed injection and auxiliary services (1,2).

5. Waste Streams - With oxygen enrichment, gas from the furnaces contains 16 to 20 percent SO_2 at the offtakes. These units, together with the converters, supply an 8 percent SO_2 stream to the acid plants (4).

Particulate emission rates have not been reported, but are probably dependent on the size distribution in the feed. Since feed is continuously injected at high velocity into a moving gas stream, particulate loadings could be substantial.

There are not solid or liquid wastes from this process. Slag is transferred to Process No. 13 for further treatment (1,2,4).

6. Control Technology - At the operating U.S. smelter, the particulates are collected in a waste heat boiler connected to the furnace hood, and in hot cyclones and finally an ESP unit. The dust is either pelletized or directly recycled. The gas is further cleaned and used for sulfuric acid production.

7. EPA Source Classification Code - None

8. References -

1. Environmental Considerations of Selected Energy Conserving Manufacturing Process Options, Volume XIV, EPA 600/7-76-034n. U.S. Environmental Protection Agency, Cincinnati, Ohio. December 1976.

2. Advertising literature and letter, Noranda Mines Limited, Toranto.

3. Mills, L.S., G.D. Hallett, and C.J. Hewman. Design and Operation of the Noranda Process Continuous Smelter. Extractive Metallurgy to Copper. AIME. 1976.

4. Dayton, Stan. Utah Copper and the $280 Million Investment in Clean Air. Engineering and Mining Journal. April 1979.

Electric Furnace Slag Treatment

1. Function - Slag from a flash or continuous smelter contains too much copper to discard economically. Also, in flash or continuous smelting there is no way to recycle the slag formed in the converters and the anode furnaces. Among the various ways to reclaim the copper content of these slags is the use of an electric furnace. This is the procedure being used with the flash smelter now operating in the United States. Slag can also be treated by flotation, as described in Process No. 13.

In electric furnace slag treatment, coke is used to reduce sulfates and metallic copper and to reconstitute the copper as a sulfide. A molten matte is formed that can be recycled to a converter for production of copper metal; the process leaves a slag low in copper content that can be discarded.

2. Input Materials - The slags are similar to those from the reverberatory furnace (Process No. 6), the copper converters (Process No's. 9 and 10), and the fire refining furnaces (Process No. 18), except with higher copper content. Flash smelting slags contain 1 to 2 percent copper, and slags from Noranda, 10 to 12 percent copper.

Carbon electrodes, as described for electric smelting (Process No. 7) are consumed. Reported usage is 1.5 kilograms per metric ton of slag processed (1). Iron pyrites are usually added to the furnace charge to adjust sulfur content. The coke is similar to that used in electric furnace operations in other industries. High grade coal can be substituted. No data on quantities consumed are available.

3. Operating Conditions - Temperatures are maintained somewhere in the range of 1200° to 1300°C (2). Pressures are approximately atmospheric.

4. Utilities - Electric consumption is reported as 221 kilowatt-hours per metric ton of slag treated (1). There is no reported use of cooling water or air in the slag treatment furnace.

5. Waste Streams - Since this is a reducing furnace, it is expected that SO_2 in the exit gases is negligible. Carbon monoxide and particulates are present, however, including metallic fumes of zinc and other elements, and there will be some hydrogen if moisture is introduced into the furnace along with the coke. There are no reported analyses of these gases. Gas volumes are relatively small.

No liquids are discharged from this process.

Slag discharged from this treatment is primarily iron silicate, similar to the slag from the reverberatory furnace (Process No. 6). No analyses are available.

6. Control Technology - In other industries, gases from reducing electric furnaces are passed through a wet scrubber for cooling and particulate removal, and are then either burned for fuel, incinerated with no recovery of the heat, or discharged through a stack. Venturi scrubbers are normally used to cool the gas quickly and minimize the possibility of explosions. This is a preferred design. Combustion of hot gases prior to particulate removal is sometimes practiced; the gases are then cooled with water sprays and passed through an ESP for particulate removal.

Particulates will probably be sluiced into a tailings pond and discarded, since they should be low in volume. They may contain quantities of trace elements, however, and their proper disposal warrants further study.

Slags from the slag treatment furnace are discarded, with or without granulation, as outlined for the reverberatory furnace (Process No. 6).

7. EPA Source Classification Code - None

8. References -

1. Personal Communication with Mr. Paterson Elken - Spigerverket a/s. New York, New York.

2. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

Flotation Slag Treatment

1. Function - Slags from a flash or continuous smelter contain a significant amount of copper, which can be reclaimed either by electric furnace treatment, as described in Process No. 12, or by slow cooling, crushing, and flotation. The flotation method will be used to treat slags from the Noranda installation now beginning operation in this country (1).

As a molten slag cools, each constituent in the slag will solidify sequentially in an order determined by the freezing temperatures of the individual minerals. If the slag is cooled very slowly, crystals of relatively pure materials will form that are large enough to be separated by conventional concentrating procedures. Copper in the slag will form either as small particles of metallic copper or as crystals of copper-iron sulfide, both held in a matrix primarily of iron silicate.

Details of the existing U.S. process have not been released. It is believed, however, that molten slag from the Noranda furnace is to be transported while still molten to a series of deep covered pits, where over a period of days, or perhaps weeks, the slag will cool by natural conduction through the surrounding earth. When fully cooled, the slag will be reclaimed by conventional mining techniques, crushed, and concentrated. The resulting concentrate will be processed in smelting furnaces in the same manner as an ore concentrate (2).

2. Input Materials - Slag from the Noranda furnace, containing 10 to 12 percent copper, is the only known input.

To reclaim the cooled slag, explosives and concentrating reagents will be used, as described in Process No's. 1 and 2.

3. Operating Conditions - Slag is withdrawn from the smelting furnace at approximately 1200°C. The slag will cool to approximately ambient temperature after an extended period of time.

4. Utilities - It is believed that the molten slag will be transported to the slag cooling area in specially-designed vehicles, requiring diesel fuel. Whether or not slag must be heated before being added to the cooling pits has not been announced.

Reclamation of the slag will require the same utilities used for mining and concentrating, consisting of electrical energy for crushing and large quantities of water for concentrating.

5. Waste Streams - A large proportion of the slag will eventually become a waste in the form of tailings whose chemical composition is similar to slag from a reverberatory furnace (Process No. 6). Additional wastes will be created such as airborne particulates from mining and crushing and waterborne contaminants from concentrating, as described in Process No's. 1 and 2.

6. Control Technology - The flotation treatment of high copper content furnace slags does not appear to introduce additional requirements for environmental control beyond those needed for control of mining and concentrating wastes. In the existing U.S. application of this process, it is not known whether special facilities will be built to reclaim the cooled slag, or whether existing mining and concentrating facilities will be adapted to this purpose.

7. EPA Source Classification Code - None

8. References -

1. Process Announcement. Kennecott Copper Corporation.

2. Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Vol. XIV, Primary Copper Industry Report. EPA-600/7-76-034n. U.S. Environmental Protection Agency, Cincinnati, Ohio. December 1976.

Contact Sulfuric Acid Plant

1. Function - An acid plant catalytically oxidizes SO_2 gas to sulfur trioxide, and absorbs it in water to form sulfuric acid. SO_2 gas may also be controlled by DMA absorption (Process No. 15) or elemental sulfur production (Process No. 16).

Contact sulfuric acid plants are continuous steady-state processing units that are operated in other industries using SO_2 made by burning elemental sulfur. They may be used with waste SO_2 streams if the gas is sufficiently concentrated, is supplied at a reasonably uniform rate, and is free from impurities.

The heart of a sulfuric acid plant is a fixed bed of vanadium pentoxide or other special catalyst which oxidizes the SO_2. All other components of the plant are auxiliary to this catalytic converter. The other components clean and dry the stream of gas, mix the proper amount of oxygen with it (unless sufficient oxygen is present), preheat the gas to reaction temperature, and remove the heat produced by the oxidation.

The plant incorporates one or two absorbers to contact the gas with water to form the acid. If only one absorber is provided, this is described as a single-contact sulfuric acid plant. If two are provided, the second is placed between stages of the converter, and this is a double-contact plant. The second absorber allows a larger proportion of the SO_2 to be converted into acid, and thus removes more SO_2 from the gas stream if the initial concentration is high.

Thirteen of the copper smelters in this country operate contact sulfuric acid plants to treat all or part of the gases from the metallurgical operations.

2. Input Materials - Most contact sulfuric acid plants operate most efficiently with a constant gas stream that contains 12 to 15 percent SO_2. Performance almost as good can be achieved in plants that are designed for 7 to 10 percent SO_2 content. The ability of a plant to convert most of the SO_2 to sulfuric acid declines either as gas streams become weaker in SO_2 or as the flow rate or concentration becomes less consistent. A concentration lower than 4 percent SO_2 is extremely inefficient, since sufficient catalyst temperature cannot be maintained (1). Certain modifications of the process, which add heat by combustion of fuel, can provide better conversion at low SO_2 concentrations.

The gas that enters the catalyst bed must be cleaned of all particulate matter, be almost completely dried, and contain no gases or fumes that act as poisons to the catalyst. The acid plant is always supplied with special scrubbers to remove final traces of objectionable materials. Table 26 provides information on the acceptable limits of these impurities.

TABLE 26. ESTIMATED MAXIMUM IMPURITY LIMITS FOR METALLURGICAL OFF-GASES USED TO MANUFACTURE SULFURIC ACID (1)

Approximate limit, (mg/Nm^3)[a]

Substance	Acid Plant Inlet	Gas Purification System Inlet[b]
Chlorides, as Cl	1.2	125[d]
Fluorides, as F	0.25	25[e]
Arsenic, as AS_2O_3	1.2[c]	200
Lead, as Pb	1.2	200
Mercury, as Hg	0.25	2.5[f]
Selenium, as Se	50[c]	100
Total Solids	1.2	1000[g]
H_2SO_4 Mist, as 100% acid	50	-
Water, as H_2O	-	400×10^3

Notes:

(a) Basis: dry off-gas stream containing 7% sulfur dioxide.

(b) For a typical gas purification system with prior coarse dust removal.

(c) Can be objectionable in product acid.

(d) Must be reduced to 6 if stainless steel is used.

(e) Can be increased to 500 if silica products in scrubbing towers are replaced by carbon; must be reduced if stainless steel is used.

(f) Can be increased to 5-12 if lead ducts and precipitator bottoms are not used.

(g) Can usually be increased to 5000-10,000 if weak acid settling tanks are used.

Clean water is required to react with the SO_3 to form sulfuric acid. It may be necessary to deionize the water in a special ion exchange system in order to avoid excessive corrosion or to meet acid quality specifications. Steam condensate may also be used.

3. Operating Conditions - The catalyst bed operates properly only if temperatures are maintained between 450° and 475°C. Pressures do not usually exceed 2 kilograms per square centimeter. The plants are usually not enclosed in a building.

4. Utilities - Noncontact cooling water is required. At one plant producing 1500 metric tons of acid per day, about 12 million liters of water is required each day (2).

A small amount of electricity is required for pumps and blowers. This may be generated on-site in some cases, where recovery of waste heat is maximized.

In certain patented modifications, heat from combustion of natural gas is used to provide better efficiency at low SO_2 concentrations. Natural gas or oil is also required to heat any acid plant to operating temperature following a shutdown.

5. Waste Streams - Single-contact sulfuric acid plants using weak gas streams can at best absorb only 96 to 98 percent of the SO_2 fed to them. The remaining quantity passes through to the atmosphere. Efficiencies as low as 60 percent have been reported (3). In addition, it is likely that some SO_2 may be vented without treatment in some smelters since an acid plant cannot instantly change the flow to match the intermittent production typical in the copper industry. Of gas that is treated, it is reported that most absorber exit gases contain from 0.01 to 0.5 percent SO_2 (4). Total flow rates may range from 34,000 to 68,000 normal cubic meters per hour (5).

Double-contact acid plants provide a higher percentage of SO_2 removal if they are fed gas with a higher SO_2 content. Efficiencies higher than 99 percent have been reported. Exit gas SO_2 concentration is still usually within the same range as shown above, although one recently developed process claims stack emissions of less than 0.005 percent SO_2 (6).

At a Japanese smelter the exit gas from the acid plant is routed to a gypsum plant and the SO_2 concentration is less than 0.002 percent at the stack exit (7).

In sulfuric acid plants, it is difficult to prevent some loss of SO_3, in the form of a fine mist of sulfuric acid, with the absorber exit gases. This is usually 0.02 to 0.04 kilogram of SO_3 per metric ton of 100 percent acid produced.

The scrubbing columns that clean the waste gas stream create off-grade weak acid that cannot be sold. The amount is estimated as 4 to 8 liters for each 10 cubic meters of gas treated (8). Table 27 provides typical analyses for acid plant blowdown.

TABLE 27. RAW WASTE CHARACTERIZATION: ACID PLANT BLOWDOWN (2)

Parameter	Units	Plant 1	Plant 2	Plant 3	Average
pH	pH	2.0-2.5	1.8	2.0	2.0
TDS	kg/metric ton		78.5	410.	244.
TSS	kg/metric ton		0.102	3.74	1.92
SO4=	kg/metric ton	[0.99][a]	7.69	64.0	36.0
Cn-	kg/metric ton	0.0000	0.0000	0.0024	0.0008
As	kg/metric ton	0.044	0.129	0.004	0.059
Cd	kg/metric ton	0.0002	0.0014	0.0276	0.0097
Cu	kg/metric ton	0.0001	0.0018	[188.2]	0.0010
Fe	kg/metric ton	0.0014	0.0015	0.1116	0.0382
Pb	kg/metric ton	0.0051	0.0142	0.2501	0.0898
Hg	kg/metric ton	0.0000	0.0000	0.0002	0.0001
Ni	kg/metric ton	0.0000	0.0000	0.0030	0.0010
Se	kg/metric ton	0.0001	0.0000	0.0268	0.0090
Te	kg/metric ton	0.0000	0.0000	--	0.0000
Zn	kg/metric ton	0.0017	0.215	0.436	0.218
Oil and Grease	kg/metric ton	0.0000	--	0.0	0.0
Flow, 10^6	l/day	0.147	4.16	10.1	--
Production	metric ton/day	311.(62)	528.(264)	655.(393)	--
Flow/Prod	kg/metric ton	2,400.	15,800.	25,700.	14,700.

[a] Bracketed values not used in averaging computation.

In this industry, most particulate matter from gas cleaning equipment is recycled in dry form or as a water slurry back to the metallurgical processes. The small quantities of particulate removed by the acid scrubbing operations, however, are mixed with a stream of weak sulfuric acid and cannot readily be recycled. They are discharged with the acid plant blowdown.

In some sections of the country it is difficult to sell the product acid, even for less than the cost of manufacture. Therefore, it may be less expensive to neutralize and discard the acid than to absorb the costs of shipment to a distant user. Thus, the product acid can itself become a waste stream.

An acid plant does not produce solid wastes directly, but the gypsum formed in neutralization of acid can constitute a significant solid waste.

6. Control Technology - In this country the SO_2 in the tail gas from the sulfuric acid plant is not controlled. When SO_2 emissions are large, the best control may be to increase operating efficiency by adding additional catalyst stages or by adding heating equipment to maintain proper catalyst temperature. Changes in the metallurgical operations to produce a stream of higher SO_2 concentration at a more uniform rate are also good controls, if this is possible. Scrubbing of the acid plant tail gas for final SO_2 absorption is practiced in Japan to achieve very low levels.

Mist eliminators in the form of packed columns or impingement metal screens can minimize acid mist emissions. Manufacturers claim elimination of all but 35 to 70 milligrams of mist per cubic meter of gas, and the units at times perform better. To prevent formation of plumes of mist during periods of abnormal operations, however, electrostatic precipitators are often used. Better regulation of feed rate and quality also minimizes acid loss.

As frequently happens in this industry, acid plant blowdown is sometimes mixed with other waters for treatment or recycle. Table 28 lists the practices of existing smelter acid plants in 1970-71. The practices outlined for Plants 1 and 3 appear to describe the best available control technology, since by recycle to hot ESP units the heavy metals content of this waste partially returns to the metallurgical processing.

If volumes of strong acid must be neutralized, treatment with limestone followed by more precise pH adjustment with lime, and discharge to a pond for in-perpetuity storage of the resulting gypsum is the only tested and economical method of disposal.

7. EPA Source Classification Code - None

8. References -

1. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

TABLE 28. ACID PLANT BLOWDOWN CONTROL AND TREATMENT PRACTICES (4)

Plant Code	Discharge	Control and/or treatment practice
1	0	Blowdown neutralized with ammonia and used to precondition converter gases prior to hot ESP. No discharge.
2	0	2/3 of blowdown to reverb brick flue spray chamber for cooling reverb gases, other 1/3 used to precondition converter gases prior to hot ESP. Any excess is solar evaporated on slag dump. No discharge.
3	0[a]	Blowdown from packed tower used in open tower blowdown to clarifier. One-half recycled to packed tower, other half to two-stage ammonia neutralization facility. Then 2.2 l/sec to converter hot ESP for gas preconditioning and 0.6 l/sec to hot ESP for gas preconditioning (joins 0.6 l/sec DMA purge). No discharge.
4	0	Blowdown to tailings pond. Pond water recirculated to mill concentrator. No discharge.
5	0	Blowdown from new scrubbers and mist precipitators to recycle and tailings thickener underflow. No discharge.
6	0	Blowdown used in mill concentrator circuit. No discharge.
7	0	Blowdown to settling pond and either recycled or wasted. No discharge.
8	0	Blowdown to acid ponds and reused in copper precipitation leach facility. No discharge.
9	0[a]	Blowdown currently used to blend fluid-bed roaster feed. Anticipate closed circuit, but will eventually send to proposed treatment facility.
10	3.4 l/sec	Blowdown to lime pond, then to tailings pond. Eventual (8 km of ponds) discharge.
11	50-190 l/sec[a]	Blowdown to go to new treatment facility with subsequent discharge.

[a] Anticipated, practice under construction.

2. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

3. Confidential information from EPA.

4. Control of Sulfur Oxide Emissions in Copper, Lead, and Zinc Smelting. Bureau of Mines Information Circular 8527, 1971.

5. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. Arthur G. McKee & Co. for U.S. DHEW, June 1969.

6. Browder, T.J. Advancements and Improvements in the Sulfuric Acid Industry. Tim J. Browder Co. San Marino, California.

7. Evaluation of the Status of Pollution Control and Process Technology - Japanese Primary Nonferrous Metals Industry. EPA Contract No. 68-02-1375, Task 36. PEDCo Environmental, Inc. Cincinnati, Ohio. July 1977.

8. Vandegrift, A.E., L.J. Shannon, P.G. Gormena, E.W. Lawless, E.E. Sallee, and M. Reichel. Particulate Pollutant System Study - Mass Emissions, Volumes 1, 2, and 3. PB-203 128, PB-203 522, and PB-203 521. U.S. Environmental Protection Agency. Durham, North Carolina. May 1971.

DMA SO_2 Absorption

1. Function - The DMA absorption process scrubs SO_2 from a stream of gas, then releases the SO_2 as a concentrated stream. The principal applications have been to concentrate streams too weak for efficient use in sulfuric acid manufacture, to absorb surges in waste gas flow that could not otherwise be handled by the acid plants, and to manufacture liquified SO_2 for sale. Sulfuric acid (Process No. 14) or elemental sulfur production (Process No. 16) may also be used to control SO_2 emissions.

Waste gases, after first being cleaned of particulate matter and dried, pass through a scrubber where most of the SO_2 is absorbed by dimethylaniline (DMA). The gases are then scrubbed with sodium carbonate to remove the remaining SO_2, then with weak sulfuric acid to reclaim the DMA in the gas stream. The gases are then released to a stack. In a series of chemical operations, the DMA is recovered for recycling, and the SO_2 is recovered as dry, 100 percent SO_2 which is compressed, cooled, and stored as a liquid.

The DMA system has the advantage of being relatively insensitive to changes in SO_2 concentration of the gas stream, and to changes in gas flow rate. If part of a waste gas stream is sent directly to an acid plant at a constant rate, the DMA can handle the remaining gas, which may be of variable composition with uneven flow. The concentrated SO_2 from the DMA plant can be bled back into the acid plant stream as required to maintain a constant and higher SO_2 concentration. Thus the acid plant operates more efficiently and more of the SO_2 in the waste gas stream is recovered.

Three smelters in this country have constructed DMA absorption plants, designed to handle waste streams that contain from 1.5 to 10 percent SO_2 (1). Efficiencies of up to 99 percent removal from a 5 percent gas stream have been reported (2). Plant capacities are as high as 180 metric tons of liquid SO_2 per day.

2. Input Materials - Waste gas containing SO_2 is the principal input. Designers of the process do not recommend its use on streams weaker than 2 to 3 percent SO_2. The gases must be cleaned and dried as described for the contact sulfuric acid plant (Process No. 14).

A constant feed of soda ash (sodium carbonate) is required for this process. One smelter reports use of 16 kilograms per metric ton of SO_2 produced.

Sulfuric acid, 98 percent concentration, is used for drying and scrubbing. The same smelter reports consumption of 18 kilograms per metric ton of SO_2 produced, as well as a small loss of the expensive dimethylaniline, 0.5 kilogram per ton of SO_2.

3. Operating Conditions - Feed gas must be cooled to ambient temperatures prior to DMA absorption. Temperature in some of the regeneration steps may reach 150°C. Pressures in the waste gas stream are near atmospheric, and may

approach 3 kilograms per square centimeter in parts of the regeneration system.

4. Utilities - Electricity is normally used to drive pumps and blowers. The process is efficient in energy conversion; treatment of a 5 percent SO_2 gas stream requires about 160 kilowatt-hours per metric ton of SO_2 produced (2).

Steam is required at a rate of 1.0 to 1.5 tons per ton of SO_2 produced (2). Noncontact cooling water is required in the amount of 1250 liters per metric ton of SO_2 (3). A small amount of process water is needed to compensate for purge and evaporation.

5. Waste Streams - Exit gas contains 0.05 to 0.3 percent SO_2 and no particulate matter. Temperatures are approximately ambient. The DMA process adds only an insignificant quantity of carbon dioxide to the stream, and very small amounts of DMA or its decomposition products may escape the third stage of scrubbing.

The waste gas stream may carry with it an entrained mist of dilute sulfuric acid from the third stage.

This process requires scrubbing of the gas stream in a weak sulfuric acid column and thus may produce a liquid waste blowdown stream similar to that from a sulfuric acid plant. Normally, however, the same scrubber is used to treat gases that feed both the acid plant and DMA system.

A liquid waste, continuously purged from the DMA process, consists of water, sodium sulfite or bisulfite, and sodium sulfate. The quantity is about 18 kilograms per metric ton of SO_2 produced, when treating gas with 5 percent SO_2 content. The stream typically contains about 4.5 percent dissolved solids, 25 milligrams DMA per liter, and 18 milligrams suspended solids per liter, with a pH around 5.8 (1).

The process produces no solid wastes.

6. Control Technology - Following DMA absorption, further treatment of the waste gas stream for SO_2 removal is not normally required. An electrostatic precipitator is usually installed to eliminate acid mist carryover.

If a separate dryer is used for DMA gas treatment, disposition of the blowdown would be the same as that for the sulfuric acid plant blowdown. Best available control technology is to neutralize this stream and recycle it as coolant to a hot ESP unit, thus returning the metals content to metallurgical processing.

The purge stream from the DMA process is the only waste of this character generated by the primary copper industry. It is a clear stream with a BOD and a COD and is quite concentrated with nonrecoverable minerals. Each of the three operating DMA installations handles the purge stream differently. One adds it to the concentrator circuits; one mixes it with the acid plant blowdown, which is in turn sent to a hot ESP unit; the third uses activated carbon to absorb the DMA content, then uses it as part of a fluid-bed wet feed blending, which returns it directly to the metallurgical processing. This last alternative may be the best control technology, with or without activated carbon absorption. The sodium may then combine into the slag where it will not increase alkali content of the concentrator water, thus reducing potential of recycle. An excess of sodium salts may plate out in a hot ESP unit. Further study to establish the best disposition of this stream is indicated.

7. EPA Source Classification Code - None

8. References -

1. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

2. Fleming, Edward P. and Fitt, T. Cleon. Liquid Sulfur Dioxide from Waste Smelter Gases. I&EC. Vol. 42, No. 11. pp. 2253-2258. November 1950.

3. Halley, J.H. and McNay, B.E. Current Smelting Systems and Their Relation to Air Pollution. Arthur G. McKee and Company. San Francisco. September 1970.

Elemental Sulfur Production

1. Function - Sulfur dioxide from a waste stream can be converted into elemental sulfur by one of several methods. Other SO_2 removal methods are sulfuric acid production (Process No. 14) and DMA absorption (Process No. 15). Sulfur is easier to store than sulfuric acid and is less expensive to transport. Although the market is also better than for acid, the sulfur now produced by this process is not economically competitive with mined sulfur from the Texas coast.

All variations of the process use high temperatures to oxidize methane to carbon dioxide and water, while simultaneously reducing the SO_2 to sulfur. All use special catalysts and are sophisticated multi-step processes, efficient in energy utilization. Like the ammonia plants or oil refinery units they resemble, sulfur plants are most efficient as large-capacity installations.

None of the smelters in this country now include sulfur production facilities, although one plant is being constructed.

2. Input Materials - Gas must enter the process at constant flow rate and composition. The gases must contain 5 to 7 percent SO_2 (1) and must be free from particulate matter and metal-containing fumes.

Methane in the form of natural gas is added in the stoichiometric ratio of 1 kilogram to each 8 kilograms of SO_2. Additional natural gas is required as fuel.

3. Operating Conditions - Although temperatures and pressures differ in the various process modifications, most operate between 1000° and 1500°C at pressures less than 25 kilograms per square centimeter. One variation requires 1250°C for proper equilibrium (2). The equipment is not normally enclosed in a building.

4. Utilities - Natural gas fuel is assumed for most designs, and electricity is required for pumps, blowers, and compressors. One variation incorporates electrostatic precipitators as integral components, which require electric power. No quantitative utility estimates have been reported.

Cooling water is required for portions of the process.

5. Waste Streams - All these processes claim removal of more than 90 percent of the SO_2 from the gas stream, and one claims up to 95 percent. The waste gas stream can therefore be expected to contain no more than 0.7 percent SO_2. Slight emissions of H_2S gas may occur in some of the process variations.

No liquid wastes are expected from this process. The water formed by the reaction normally escapes by evaporation into the waste gas stream.

This process produces no solid wastes.

6. Control Technology - The only further control of the waste gases from this process is wet scrubbing, as described in connection with the reverberatory furnace (Process No. 6).

7. EPA Source Classification Code - None

8. References -

1. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation, Park Ridge, New Jersey. 1972.

2. Fleming, E.P. and T.C. Fitt. High Purity Sulfur from Smelter Gases. Industrial and Engineering Chemistry. Volume 42, No. 11. March 1950. pp. 2249-2253.

Arsenic Recovery

1. Function - Much of the arsenic present in a copper ore concentrate will be volatilized in the roasting and smelting processes, and will appear as arsenic trioxide in the dusts collected from the electrostatic precipitators and other particulate removal equipment. One smelter treats those dusts to extract arsenic for sale. Since demand for arsenic as a commercial item is very small, this one smelter satisfies much of the U.S. demand for this material. The balance is met by imports.

The recovery process consists of placing the collected dusts in a Godfrey roaster, a small special heated enclosure, in which they are heated until the arsenic trioxide vaporizes. The vapors are condensed in chambers, and are then resublimed and condensed to yield an arsenic trioxide product more than 99 percent pure. Arsenic metal is also occasionally produced by reducing the oxide with carbon in an atmosphere deficient in oxygen (1).

All these operations are batch-type and are done on a small scale.

2. Input Materials - Flue dusts from multiple-hearth roasters and reverberatory furnaces are the principal input. Dusts of high arsenic content from other smelters were also used at one time, but are no longer accepted by this smelter. Flue dusts are charged into the furnace along with a small amount of pyrite to minimize conversion to arsenites (1).

Charcoal in small quantity may be used for arsenic metal production.

3. Operating Conditions - Arsenic trioxide is assumed to be completely vaporized from the dusts when the temperature reaches 650° to 700°C. It recondenses in the cooling chambers at around 200°C (1). Atmospheric pressures are used.

4. Utilities - Gas-fired burners are used to heat the charge, and noncontact cooling water to assist in condensing. No quantities have been reported.

Water is used to wash down dust and spills within the plant.

5. Waste Streams - Because there is no mechanical movement of material within the Godfrey roaster, few particulates are generated during the operation. Fugitive dusts are generated during the handling of the dry materials.

The gas stream from the roaster contains carbon dioxide and water vapor, and may contain small amounts of SO_2 and arsenic fumes. No analysis has been reported.

A water waste is generated by daily washdown of the plant to remove settled dusts from materials handling. Table 29 gives the analysis of this water.

TABLE 29. ANALYSIS OF ARSENIC PLANT WASHDOWN WATER (2)

Parameter	Concentration mg/l
As	310.
Cu	88.4
Zn	37.0
Pb	7.7
Cd	1.05
Hg	0.0003
Se	0.04
Te	0.43
Ni	0.75
Fe	9.4
$SO_4^=$	340.
Cn^-	0.01
Oil and grease	0.04
pH	3.8 to 4.4

No solid wastes are generated by this process.

6. Control Technology - Fugitive dust emissions in and from the plant building are controlled by the use of fabric filter baghouses on ventilating air streams.

Effluent process gas streams are currently routed through an electrostatic precipitator before being vented to a tall stack. After treatment for arsenic removal, the remaining dusts are returned to the smelting furnace. In the near future, a fabric filter will be installed to remove particulate from the waste gas.

The washdown from this plant mixes with another waste stream and discharges to a pond. Table 29 indicates that up to a kilogram of arsenic may enter the pond each day from this source. The degree to which it becomes soluble has not been reported.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Primary Copper, Lead, and Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category (Draft). Contract No. 68-01-1518. U.S. Environmental Protection Agency. Washington, D.C. December 1973.

Fire Refining and Anode Casting

1. Function - Impure or "blister" copper from the converters must be refined to remove impurities. This is partially accomplished by fire refining, which is the last major process that occurs at a copper smelter.

Blister copper is placed in a fire refining furnace, a flux is usually added, and air is blown through the molten mixture. This blow oxidizes most of the remaining sulfur, vaporizes some impurities and converts others into a slag. The mixture is then "poled" with wooden logs or otherwise treated to reduce the excess oxygen in the mixture. The copper is then poured into molds and cooled with water sprays or by immersion in a tank of water. The resulting anodes are sent to an electrolytic refinery for further processing.

A small percentage of the copper may be subjected to more complete fire refining to produce ingots or special castings for direct sale. This fire refined copper is used for manufacture of alloys and other special purposes, and contains no impurities other than oxygen in significant amounts. Anode copper is less completely refined, but is more than 99 percent pure. The general range of analysis is shown in Table 30.

2. Input Materials - Copper from the converting operation (Process No's. 9 and 10) is the principal input, usually charged into the fire refining furnace while still molten.

Various slag-forming fluxes may be added. These include silica sand and sodium carbonate.

Wooden poles are still occasionally used for the reducing step of the process. The wood decomposes when thrust into the molten copper, producing a variety of carbonaceous products that remove oxygen from the mixture. Instead of wood, most smelters now use hydrogen, natural gas, or ammonia for reduction.

The casting molds are sprayed with a mold dressing of silica flour or potassium alum to keep the castings from sticking (1).

3. Operating Conditions - Temperature in the furnace is around 1100°C. Pressure is atmospheric.

4. Utilities - If molten blister copper is charged to the furnace, additional fuel is required only in small amounts. Gas or oil is used for heating, or to melt the charge if cold feed is used. In a plant producing 91,000 metric tons of copper per year, fuel consumption for this process has been estimated at 8600 kilocalories per hour of operation (1).

Compressed air is used to oxidize the molten mixture in the furnace. No quantities have been reported.

TABLE 30. GENERAL RANGE ANALYSIS OF ANODE COPPER[a] (1)

Constituent	Content, % weight
Copper	99.0-99.6
Oxygen	0.1-0.3
Sulfur	0.003-0.01
Arsenic	0.003-0.2
Antimony	0.001-0.1
Bismuth	0.001-0.01
Lead	0.01-0.2
Nickel	0.01-0.2
Selenium	0.01-0.06
Tellurium	0.001-0.02
Gold	3.4-102.6[b]
Silver	68-3080[b]
Platinum	N.A.
Palladium	N.A.

[a] Extremes omitted

[b] g/metric ton

N.A. - not available

Water is used for direct cooling of the casting machine and the copper anodes. This is usually a recirculated stream or is reclaimed water from combined sources. Quantities are shown in Table 31 for five smelters.

5. Waste Streams - Gases from the fire refining furnace may contain fumes of zinc and cadmium (2). Concentration of SO_2 has been estimated at 0.38 kilogram per metric ton of copper treated (3). There are no recorded data giving the quantity of this waste gas, but particulate loading has been reported as 5-20 kilograms per metric ton of copper produced (4). Gas temperature is about 1000°C (5).

The water used for anode cooling is reported to pick up additional amounts of arsenic, copper, and zinc, and also to pick up aluminum and chlorides, probably from mold dressing compounds. Table 32 lists the data reported for one anode cooling operation. The "net change" represents the difference between inlet and outlet concentrations.

There are no solid wastes from this process. All slags are returned to the metallurgical processing.

6. Control Technology - No control of waste gas from the fire refining process is being exercised by any of the operating copper smelters. Apparently it is assumed that this is one of the cleaner gas streams from pyrometallurgical operations because of the relative purity of the input copper.

Table 33 lists the controls of contact cooling water being practiced by the domestic smelters. This list includes water used for cooling of both anodes and blister copper direct from the converter.

7. EPA Source Classification Code - 303-005-05

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

3. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

4. Compilation of Air Pollutant Emission Factors. AP-42. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. March 1975.

5. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

6. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-74/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

TABLE 31. WATER REQUIREMENTS FOR COPPER REFINERIES (5)

Plant	Water intake, liters per metric ton of metal produced	Water consumed (Intake minus discharge), liters per metric ton of metal produced
A	4,000	4,000
B	9,000	700
C	13,000	1,200
D	3,000	1,900
E	6,000	0

TABLE 32. WASTE EFFLUENTS FROM ANODE COOLING WATER (6)

Parameter	Net change, mg/l	Net loading	
		kg/day	kg/metric ton
Chloride	8.7	7.8	0.029
Aluminum	0.12	0.11	0.0004
Arsenic	0.01	0.01	<0.0001
Copper	8.53	8.07	0.030
Zinc	0.25	0.24	0.0009
Flow, 10^6 l/day	0.95		
Production, metric ton/day	265		

Source: RAPP.

TABLE 33. CONTACT COOLING WATER CONTROL AND TREATMENT PRACTICES (6)

Plant code	Discharge	Control and/or treatment practice
1	0	Anode casting: water in closed circuit with cooling tower, cooling tower blowdown joins blowdown from wire-bar casting cooling tower blowdown, entire blowdown to side-stream filter, anticipate total water recycle.
2	0	Anode casting: water directly reused in mill concentrator circuit. No discharge.
3	0	Anode casting: water collected in mill tailings thickener, all flow recycled (with some evaporation) to mill concentrator. No discharge.
4	0	Blister cake cooling: air cooled with some water spray; spray water totally recycled from cooling pond. No discharge.
5	Intermittent	Fire-refined (cathode) - shape casting: water mostly recycled, with small intermittent discharge.
6	0	Fire-refined casting: water to thickener, overflow recycled. No discharge.
7	0	Anode casting: water in closed circuit with cooling tower, blowdown to evaporation pond. No discharge.
8	0	Anode casting: water in closed circuit with cooling tower, blowdown reused in mill concentrator. No discharge.
9	0	Anode casting: water to tailings thickener, reused in mill concentrator. No discharge.
10	0	Anode casting: water all used in mill concentrator circuit. No discharge.
11	0	Anode casting: water in closed circuit with 100 percent circulation. No discharge.
12	5670 m^3/day	Anode casting: water collected in slag settling pond, part is recirculated for slag granulation 53,000 m^3/day. Remainder 5700 m^3/day discharged to tailings ponds. Eventual (8 km of ponds) discharge.

TABLE 33. (continued).

Plant code	Discharge	Control and/or treatment practice
13	18 l/sec	Anode casting: once-through water, part used for shot copper cooling, remainder discharged.
14	~340 m^3/day (125 l/sec, 45 min/day)	Shot copper cooling: Intermittent flow, all discharged. Plan to treat water in proposed treatment facility with anticipated discharge.
15	0	Blister cake cooling: water consumed during spraying and air cooling. No discharge.

Electrolytic Refining

1. Function - Although copper produced at a smelter contains less than 1 percent impurities, this is too much to meet most of today's quality specifications. The electrolytic refinery reduces the impurities to approximately 0.05 percent.

The refining is done by passing a direct current of electricity through two copper electrodes that are immersed in a bath of acidic copper sulfate solution. The anode is a casting of impure copper from the smelter, and the cathode is a "starting sheet" stripped from a previously refined block of electrolytic copper. The electric current causes the copper to dissolve from the anode and deposit at the cathode. Impurities either will not dissolve in the electrolyte, or will not plate out at the cathode, so they collect either as slimes in the bottom of the cell or as soluble ions in the electrolyte.

Fourteen electrolytic refineries are operating in the United States. Five are located near a copper smelter, and the others are distant from smelters.

2. Input Materials - The principal input is the anode castings from copper refining. About 85 percent of the anodes in use at any one time are directly from the smelter. The remainder are made at the refinery by melting and recasting partially electrolyzed anodes.

The electrolyte is sulfuric acid, which is either fresh acid or acid reclaimed from the electrolyte purification process (Process No. 20).

Various additives are used to ensure a smooth deposit at the cathode. Chlorides are added to cause silver to precipitate into the slimes.

3. Operating Conditions - Electrolytic cells are normally maintained at 60° to 65°C (1). Pressures are atmospheric.

4. Utilities - Electric power is the only source of energy. Approximately 175 to 220 kilowatt-hours are required to produce a metric ton of cathode copper (2). The direct current required for the cells is produced within the refinery by rectifiers or motor-generator sets. Additional electricity is required for the auxiliary materials handling equipment.

Water is used for washing the cathodes as they are removed from the cells. In most refineries, this is specially treated water, usually steam condensate, since untreated water contains minerals that affect the quality of the product. This same water is used for make-up to the electrolyte system to replace that lost in purge and evaporation.

5. Waste Streams - The only pollution of the air by an electrolytic refinery is a fine mist of sulfuric acid reported to be created near the electrodes. Data on this source of pollution are not available.

Most refineries reclaim the copper from impure solutions (see Process No. 20), but two do not, and therefore create a substantial liquid waste directly from the electrolytic cells. Table 34 gives the range of composition of the electrolyte solution, along with the composition of the refined copper and the slime that is recovered from the bottom of the cells.

Slime is periodically cleaned from the cells and processed for recovery of the gold, silver, and other valuable elements (see Process No's. 22 and 24). Because this slime represents a product of considerable value to the copper industry, procedures at most smelters are designed to place as much of these valuable elements as possible into the anode copper.

In any plant that handles highly corrosive liquids in large quantities, there are leakages, spills, and occasionally major discharges, frequently not expected and normally not included in waste tabulations.

No solid wastes are produced by an electrolytic refinery.

6. Control Technology - Of the two refineries that do not reclaim the impure electrolyte solution, one treats this stream separately by placing it in a lined pond and allowing it to evaporate to dryness. Climatic conditions at this site make this procedure workable. The other refinery follows a practice often used in the copper industry and mixes the solution with other wastes into a tailings pond, where lime is added to neutralize the acid. This refinery is also in an arid section of the country. Both refineries report no discharge into public waters. Ultimate disposal of the solids from these evaporations has not been reported.

Most refineries have demonstrated an economic benefit from the reclamation and partial recycle of spent electrolyte; this represents the best available control technology (see Process No. 20).

There are usually no controls specifically designed to handle spills, leakages, and accidental discharges of electrolyte.

7. EPA Source Classification Code - 303-005-05

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

TABLE 34. GENERAL RANGE ANALYSIS OF ELECTROLYTE, REFINED COPPER, AND ANODE SLIME[a] (2,3)

Constituent	Electrolyte, g/l	Refined copper, % weight	Raw slime, % weight (dry basis)
Sulfuric acid	170-230		
Copper	45-50	99.95	20-40
Oxygen		0.03-0.05	
Sulfur		0.001-0.002	2-6
Arsenic	0.5-12	0.0001-0.001	0.5-4.0
Antimony	0.2-0.7	0.0002-0.001	0.5-5.0
Bismuth	0.1-0.5	0.00001-0.00002	tr.
Lead		0.002-0.0010	2.0-15.0
Nickel	2.0-20.0	0.0001-0.002	0.1-2.0
Selenium		0.0003-0.001	1.0-20.0
Tellurium		0.0001-0.0009	0.5-8.0
Gold		0.68-0.242[b]	1714-10286
Silver		1.71-17.1[b]	34285-274283
Platinum		tr.	N.A.
Palladium		tr.	N.A.
Iron		tr.	0.1-0.2

[a] Extremes omitted.

[b] g/metric ton.

tr. = trace.

N.A. = Not available.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

Electrolyte Purification

1. Function - In operation of the electrolytic cells in a refinery, certain impurities become dissolved in the electrolyte solution. If a portion of the electrolyte is not removed from the circulating stream, concentrations of these impurities will become so high that they begin to deposit at the cathode with the refined copper. In most cases, the purge stream is processed to recover some of its constituents.

All but two of the refineries in this country remove the copper from the purge stream. This is done in special "liberator" electrolytic cells that use insoluble lead anodes and sheets of copper as cathodes. The copper and frequently some of the impurities deposit on the cathode. The plates of copper are returned to the metallurgical processing either within the refinery or in the smelter, depending on quality. Some of the remaining impurities collect in the liberator cells as a sludge.

A few refineries recover a portion of the sulfuric acid from the purge stream by use of dialysis equipment. The dialyzers provide a partial separation of the acid and produce a stream in which impurities are more concentrated. The acid is returned to the electrolyte circulation.

Effluent from the liberator cells or the dialysis equipment may be concentrated further by removing water in vacuum evaporators. Concentration of the acid produces a sludge, which has a high concentration of nickel sulfate and usually contains iron and zinc. This sludge can be filtered out, and then part of the acid can be returned to the electrolyte system, or it may be discarded or sold.

Various refineries may practice all, part, or none of these treatments. Three refineries recover nickel. One refinery consumes all spent electrolyte in an associated chemical operation (1).

2. Input Materials - The input is the purge stream from the recirculating electrolyte. The range of analysis is given in Table 34 (Process No. 19). This shows it to be a stream of warm, concentrated acidic copper sulfate solution, also containing nickel, arsenic, antimony, and bismuth. Smaller quantities of iron, cobalt, zinc, lead, selenium, tellurium, and other elements are also found in the stream.

3. Operating Conditions - Temperatures are less than 100°C and pressures are atmospheric, except in some evaporation operations (2).

4. Utilities - Electricity is used to drive pumps and mechanical equipment, and to operate the liberator cells. Since the average concentration of salts in the liberator electrolyte is much less than in the main electrolytic cells, the liberator requires 2 to 5 times as much current to remove the same amount of copper. Usage is reported as 350 to 700 kilowatt-hours per metric ton (1).

Steam may be required for vacuum production, and fossil fuels may be used for direct-fired evaporation.

5. Waste Streams - The principal characteristic of the waste streams from electrolyte treatment is that, combined, they must contain almost all the arsenic, antimony, and bismuth that comes in with the anode copper (3). Some of these elements may be returned to the smelter with liberator cathodes, even though there is no way to dispose of them there. Examination of Table 30 (Process No. 18) shows that a ton of arsenic enters the electrolytic refinery with as little as 500 tons of anodes, and the best analysis shown in this table would provide a ton of arsenic waste for each 40,000 tons of copper.

Some of the arsenic is known to escape from the second stage of the liberator cells as arsine (AsH_3) (4). This very poisonous gas can accumulate to dangerous levels if the liberator cells are not well ventilated. Arsine will slowly oxidize in the atmosphere to arsenic trioxide and water. Quantities apparently have not been measured. This is also the only reference to arsenic in a waste stream from this process.

Unless all of these elements are returned to the smelter with the liberator cathodes, the arsenic, antimony, and bismuth must exit with a purge of electrolyte acid. It appears that accumulation of these elements must result in either continuous or occasional disposal of a quantity of "black acid", regardless of the extent of electrolyte treatment employed.

In some refineries evaporated water from the electrolyte constitutes another waste stream, which usually is mixed with volumes of steam condensate and direct cooling water in barometric leg discharge devices. Table 35 provides an analysis from such a source.

No solid wastes are discharged from this process.

6. Control Technology - Arsine formed in the liberator cells can be readily oxidized or can be scrubbed to form a liquid waste. Best control technology cannot be evaluated unless the order of magnitude of the quantity being released is known. If the amount is fairly large, it should be possible to design an oxidation process that could recover this as dry arsenic trioxide.

If it is possible to sell or give away the black acid to the fertilizer industry, as has been reported, the impurity elements would be transferred into the gypsum ponds from phosphate rock treatment. This would eliminate disposition in local tailings ponds, which are already loaded with metal ions from other sources. The neutral to acidic nature of phosphate ponds may cause a greater degree of precipitation of arsenic and antimony than would occur in the alkaline water designed to precipitate copper. On the other hand, phosphate ponds may already have a heavy load of radium, and are usually located in an area of greater precipitation than copper smelters.

TABLE 35. WASTE EFFLUENTS FROM $NiSO_4$ BAROMETRIC CONDENSER (1)

Parameter	Intake, mg/l	Discharge, mg/l	Net change, mg/l	Net loading kg/day
pH	6.5	6.6		
Alkalinity	90			
COD	750	450	neg	
Total Solids	21.080	24,000	2,920	
Dissolved Solids	21,060	24,000	2,920	
Suspended Solids	18	18		
Sulfate (as S)	1,722	1.060	neg	
Arsenic	<0.010	<0.010		
Cadmium	<0.20	<0.20		
Copper	<0.20	<0.20		
Iron	<0.50	1.30	<1.3	<15
Lead	<0.50	<0.50		
Nickel	<0.50	<0.50		
Zinc	<0.20	0.48	<0.48	<5.4
Flow, 10^6 l/day		11.4		
Production, metric ton/day		415		

For the effluent from a vacuum evaporator condenser, the best control technology is to avoid overloading the evaporator. Because of the low volatility of sulfuric acid and other components of this stream, evaporation of the water should be easy if the evaporator is properly designed, instrumented, and operated.

7. EPA Source Classification Code - None

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-74/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

4. Trace Pollutant Emissions from the Processing of Metallic Ores. PEDCo-Environmental Specialists, Inc. August 1974.

Melting and Casting Cathode Copper

1. Function - Refined copper from the electrolytic cells is melted and recast into the shapes required by fabrication industries. There is usually also a final adjustment of the oxygen content of the finished product.

Special equipment used for these operations ranges from direct-fired reverberatory furnaces to continuous casting machines. Electric arc and induction furnaces may be used to melt or hold the molten copper. The trend in this process is toward continuous or semicontinuous equipment to provide closer control of product quality and to minimize energy requirements.

2. Input Materials - The principal input is cathodes from the electrolytic cells. These are washed free of electrolyte and slime prior to delivery to this process.

Mold dressings such as bone ash may be used in some operations. For production of certain grades of copper, special oils, graphite, and phosphorous-copper alloys may be added at various stages in the process.

Use of reverberatory furnaces for this process requires addition of a flux and possibly a "poling" operation (1). This modification is comparable to fire refining and anode casting (Process No. 18).

3. Operating Conditions - Depending on the process details, temperatures range from 1150° to 1215°C (2). Pressures are atmospheric. Special reducing atmospheres may be used in some operations. Open molds are usually cooled with water sprays to around 150°C.

4. Utilities - Electricity or fossil fuel may be used for melting. The newest electrical furnaces are reported to operate at high thermal efficiencies; power consumption is rated at 250 to 300 kilowatts for maintaining a molten charge of 55 to 90 metric tons of copper in an electric arc furnace (3).

Electricity is used to power materials handling and casting equipment.

Both contact and noncontact cooling waters are used to cool the casting equipment and the cast shapes. One refinery reports a water usage of 320,000 liters per day (4).

5. Waste Streams - Reverberatory furnaces, still occasionally used for refined copper melting, produce a gaseous discharge to the atmosphere; the quality of this emission has not been reported.

Table 36 provides the analysis of water used for cooling the refined copper shapes at two refineries. Another report showed an increase in chlorides of 58.6 grams per liter (3), but the origin of this ion was not defined.

TABLE 36. ANALYSIS OF WATER USED TO COOL REFINERY SHAPES (4)
(Concentrations in mg/l)

Parameter	Plant X		Semicontinuous cake casting	Plant Y	
	Inlet water	Wirebar cooling		Inlet water	Wirebar cooling recycle
pH	7.6	7-8	8.	7.1-7.6	8.0-8.4
TDS	1430.	1250.	1400.	0.2	0.1
TSS	0.0	12.5	0.0	0.5	0.4
SO_4	240.	240.	270.		
As	0.001	0.001	0.001	0.001	0.001
Cd	0.001	0.001	0.001	0.0008	0.0021
Cu	0.30	0.69	0.18	0.021	3.5
Fe	0.02	0.13	0.04	1.2	1.7
Pb	0.007	0.007	0.003	0.078	0.068
Hg	0.00350	0.00425	0.0001	0.00004	0.00004
Se	0.001	0.001	0.001	0.040	0.040
Te					
Zn	0.001	0.067	0.001	0.35	0.088
Oil and grease	0.0	2.0	0.0	0.14	0.1

There are no solid wastes from this process.

6. Control Technology - There is no control of air emissions from a melting or casting operation, and specific control is probably not required.

Water from this process is often cooled prior to discharge, but is not usually otherwise specially treated.

7. EPA Source Classification Code - 3-03-005-008

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Trace Pollutant Emissions from the Processing of Metallic Ores. PEDCo-Environmental Specialists, Inc. August 1974.

4. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

Slime Acid Leach

1. Function - The first step in treatment of slimes from the cells of an electrolytic refinery is removal of the copper. This may be by direct roasting (Process No. 24), or the slimes may be first leached with acid to extract a portion of the copper prior to the roasting step. The acid leach is accomplished in a pressure filter, through which sulfuric acid is circulated. Copper dissolves in the acid as a solution of copper sulfate. This solution is either mixed with the electrolyte in the refinery cells (1), or with the electrolyte purge to the liberator cells, or may be used for copper sulfate production (Process No. 23).

2. Input Materials - The primary input is the slime from the electrolytic cells (Process No. 19), which may contain 20 to 40 percent copper (2). Small particles of metallic copper will be present.

Sulfuric acid is the leach solvent. Concentration and quantity of the acid vary with the slime composition.

3. Operating Conditions - There is normally no heating of the circulating solution, but chemical action may cause a slight temperature rise above ambient. Pressures are atmospheric to slightly higher, not exceeding one kilogram per square centimeter.

4. Utilities - A small quantity of electricity is used to power pumps for acid circulation. Water or steam concentrate is used to wash the leached slimes prior to transferring them to the roaster.

5. Waste Streams - A minor evolution of SO_2 in this process is due to the reaction of copper metal with the acid (3).

Except for accidental spills or pump leakage, there are no liquid or solid wastes. All materials are transferred to other processes.

6. Control Technology - If this were a larger-scale process, control of SO_2 by blending with other streams (if available) or by scrubbing would be the best control technology. Since quantities are small, none of the refineries control this emission except by local ventilation.

7. EPA Source Classification Code - None

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-74/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Leigh, A.H. Precious Metals Refining Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

$CuSO_4$ Precipitation

1. Function - The function of this process is to precipitate copper sulfate in crystal form as a marketable by-product. The solution from water or acid leach constitutes part or all of the source. Copper powder is first added if there is excess acidity, and excess water is evaporated. When the mixture cools, crystals of copper sulfate form. The concentrated liquor either returns to the electrolytic cells or is transferred to chemical operations for the manufacture of other products. The crystals may be heated to remove water of hydration prior to sale.

2. Input Materials - The input is the leached solution from the Slime Acid Leach (Process No. 22), containing copper sulfate and sulfuric acid, or from the Slime Water Leach (Process No. 25), containing copper sulfate in water. Copper powder may also be added.

3. Operating Conditions - Atmospheric evaporators are usually used, with boiling temperatures less than 125°C. Crystallization occurs in atmospheric vessels. The crystals may be heated as high as 600°C after separation from the mother liquor if anhydrous copper sulfate is being produced (1).

4. Utilities - This is primarily a chemical type process, using either direct gas-fired or steam-heated evaporation equipment, noncontact cooling water for crystallization, and electricity for solution transfer and auxiliaries. Utility usage is not reported, but quantities are small.

5. Waste Streams - Use of copper powder for neutralizing excess acid will cause a slight evolution of SO_2, which will be stripped into the atmosphere during evaporation (2).

Water evaporated from the solution will condense as a wastewater, or will be lost into the atmosphere if direct-fired evaporators are used. Some carryover of entrained solution could occur. There are no reports of the waste from this source.

The process produces no solid wastes.

6. Control Technology - No controls are currently associated with this process. If quantities of SO_2 evolution were greater, scrubbing or mixing with another stream for combined SO_2 treatment would provide adequate control.

There is no report on the disposition of water from this source.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Leigh, A.H. Precious Metals Refining Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

Slimes Roasting

1. Function - Roasting of slimes from the cells of an electrolytic refinery allows removal of the copper content. A portion may be removed by acid leach of the slimes (Process No. 22). Heating the slimes in a strong acid environment converts the remaining copper to soluble copper sulfate, which can be removed by a subsequent water leach process (Process No. 25) (1). Roasting also converts some of the silver and tellurium to soluble salts and volatilizes some of the selenium.

2. Input Materials - The principal input is the slime materials, either direct from the electrolytic cells or as residue from acid leach.

Fluxes in the form of sulfuric acid and sodium sulfate are used to ensure complete reaction of almost all the copper present in the slime, which may be as much as 40 percent by weight of the slimes (2). One report gives the sulfuric acid consumption as 1.74 kilogram of acid per kilogram of slime treated (2).

Muds from the scrubber (Process No. 27) are also recycled to this roaster (3).

3. Operating Conditions - Temperatures in the roaster are maintained between 540° and 650°C. Pressures are atmospheric (1).

4. Utilities - Gas or oil is used for heating, and electricity for driving mechanical equipment. Quantities are not large, because of the small scale of this equipment.

5. Waste Streams - The gas leaving the roaster contains highly mineralized particulates and fumes. Roasting breaks down silver and copper selenides, releasing SeO_2 (1). Arsenic, tellurium, and trace amounts of lead also are present as fumes. The stream contains SO_2 and dusts, which consist of all the elements present in the slime. This gas stream normally passes to the scrubber (Process No. 27), but any loss can represent a hazardous waste. No analyses of this stream have been reported.

No liquid wastes are generated.

Solids from the roaster contain the most valuable metals, and are usually carefully transferred to the water leach equipment (Process No. 25). There is no solid waste.

6. Control Technology - Proper transfer of the highly mineralized gases from this process to the scrubber is the best control.

7. EPA Source Classification Code - None

8. References -

1. Leigh, A.H. Precious Metal Recovery Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

Slime Water Leach

1. Function - The objective of this process is to reprecipitate all the silver and tellurium that has been made water-soluble in the roasting process, and to dissolve and separate all the soluble copper (1).

Powdered copper is added to roasted solids in calculated quantity (2). The mixture is then slurried with water in a tank, and by a cementation reaction, the silver and tellurium are precipitated. The mixture is allowed to stand to cause these reactions to approach completion and to allow the solids to settle. The liquid is then decanted off, and the slurry is filtered. The liquid solution of copper sulfate returns to the electrolytic cells or is used for copper sulfate production (Process No. 23). The filter cake is transferred to the Doré Furnace (Process No. 26) (3).

2. Input Materials - Roasted slime from Process No. 24 is the principal input. Powdered copper in slightly less than stoichiometric proportions is added. Water is also added.

3. Operating Conditions - The temperature in the leach tank is less than 100°C, but is not carefully controlled (3). Pressures are atmospheric, rising to less than 3 kilograms per square centimeter during filtering.

4. Utilities - No external heat is added to this process. The hot solids from the roaster add incidental heat.

Either deionized water or steam condensate is used to prevent introduction of foreign elements into the electrolyte solution.

5. Waste Streams - Except for accidental spills, no wastes are generated by this process.

6. Control Technology - None

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

3. Leigh, A.H. Precious Metals Refining Practice International Symposium on Hydrometallurgy. Chicago, Illinois. Feburary 25 - March 1, 1973. pp. 95-110.

Doré Furnace

1. Function - This process separates the trace elements contained in the slimes into several distinct fractions, each of which is either sold or further treated. The most valuable fraction is a Doré metal, consisting primarily of silver, gold, and the platinum group metals.

The equipment is a special small reverberatory furnace, which removes groups of elements in separate slag-producing steps. The filter cake from the water leach process is mixed with a silica flux, charged into the furnace, and heated. A slag forms, containing primarily the lead, iron, arsenic, and antimony (1). This "sharp slag" is withdrawn and can be sent for further processing to a lead smelter. Sodium salts are then added to the furnace, and a soda slag forms. This slag contains selenium and tellurium and any residual arsenic and antimony (2) and is further treated (see Process No. 28). An oxidative slag is then formed by blowing air through the molten metal (3), removing bismuth and any remaining copper. This slag is returned to the copper smelter. At least one refinery performs a final cleanup using Portland cement, which returns to the Doré furnace at the start of the next charge.

The Doré metal that remains may be sold to a specialty processor, or may be further refined (see Process No. 30). Table 37 gives the approximate range of analysis.

Table 37. DORE METAL ANALYSIS (2)
% Weight

Gold	8 to 9%
Silver	90 to 92%
Copper	0.5 to 1.0%
Palladium	0.16 to 0.18%
Platinum	0.05 to 0.009%
Lead	0.02%
Tellurium	0.003%
Selenium	0.00002%

2. Input Materials - Filter cake from the water leach process is the primary input. The slimes at this stage are fairly low in copper content; they contain about 18 percent water (2) and no sulfur.

Silica sand is the first flux, and a 2:1 mixture of sodium carbonate and sodium nitrate is the second. Quantities depend on the analysis of the filter cake (4). Portland cement is used in very small quantities (2).

3. Operating Conditions - Temperatures in the furnace rise as high as 1400°C. Pressures are atmospheric (1).

4. Utilities - Gas or oil fuel a Doré furnace (1,2). Compressed air is used in the third stage slagging operation. Electricity is not required except for auxiliary purposes.

5. Waste Streams - Flue gas temperatures may reach 1370°C (2). The stream may be high in particulate matter and in fumes containing selenium, tellurium, some arsenic, antimony, and lead. These are normally sent to a wet scrubber (Process No. 27). The precious metals content of the particulate matter is high enough that care is taken to collect them, but no analyses have been reported.

There are no liquid wastes from the Doré furnace.

This process produces no solid wastes if all the slags are processed or recycled as outlined above. The soda slag would be especially troublesome if it became a solid waste, since it is rich in soluble oxidized salts of arsenic, antimony, tellurium, and selenium.

6. Control Technology - Wet scrubbing of the gases for removal of particulates and fumes is the best control of this gas stream.

Care should be taken in the handling of slags from the Doré furnace to avoid secondary water pollution from this source.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Leigh, A.H. Precious Metal Refining Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

4. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency, Washington, D.C. September 1973.

Scrubber

1. Function - Gases from the slimes roaster and the Doré furnace contain particulates in quantities that justify their recovery for further processing. The gases also contain fumes, especially of selenium, which hydrolyze in the water scrubber, allowing their separation for sale.

The scrubbers are generally of the water spray type (1), with the water continuously recirculating. As solid material accumulates, periodic blowdown is performed. The amorphous selenium is often removed by flotation (2), or occasionally the blowdown is combined with the soda slag leach liquor (Process No. 28). Muds from the scrubber are recycled to the slimes roaster (Process No. 24).

2. Input Materials - Flue gases from the Doré furnace and the slimes roaster are the principal inputs.

If flotation recovery of selenium from the blowdown is practiced, methylamyl alcohol and liquid colloid glue are used as flotation reagents (2).

3. Operating Conditions - The gases entering the scrubber are extremely hot, about 1000° to 1300°C. The water sprays are at ambient temperatures (3). Pressures are near atmospheric.

4. Utilities - Water is used as makeup to replace evaporation losses and electricity is used to drive the exhaust blower. Quantities are not large.

5. Waste Streams - Gases leaving the scrubber may contain particulates and fumes that were not removed. Selenium is expected to be a major constituent.

If all the scrubbing liquor and particulates are recycled to previous operations, no liquid or solid wastes are produced.

6. Control Technology - Most refiners find it economical to install electrostatic precipitators on the scrubber effluent to remove the highly metalliferous dusts and fumes that escape collection. The use of a more efficient venturi-type scrubber would also be an acceptable control.

7. EPA Source Classification Code - None

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

2. Leigh, A.H. Precious Metals Refining Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 75-110.

3. Particulate and Sulfur Dioxide Emission Control Cost Study of the Electric Utility Industry. 68-01-1900. U.S. Environmental Protection Agency. Washington, D.C.

Soda Slag Leach

1. Function - The soda slag, the second slag removed from the Doré furnace, is rich in selenium and tellurium, both of which are marketable by-products (1). The function of this leach process is to selectively dissolve these elements from the slag (2).

The slag is leached in a tank of water, which becomes alkaline because of the sodium oxide content of the slag. Selenium and tellurium dissolve as sodium selenite and tellurite (3). The resulting solution is filtered from the insoluble components of the slag, and the solids are returned to the Doré furnace for reprocessing. The leached solution is further treated (see Process No. 29).

2. Input Materials - The soda slag from the Doré furnace is the only input.

3. Operating Temperature - Residual heat in the slag and chemical action between the slag and the water cause some temperature increase during leaching, to less than 100°C (2,4). Pressures are atmospheric during the leach, and less than 2 kilograms per square centimeter during filtration.

4. Utilities - Water is required as the leaching solvent.

The literature does not state whether supplemental heat is required during this step.

Electricity in small quantity is used to pump the leached slurry through the filter.

5. Waste Streams - There are no gas, liquid, or solids wastes from this process. All materials at this stage are valuable and are carefully handled (3).

6. Control Technology - None is required.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Leigh, A.H. Precious Metal Recovery Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

4. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

Selenium and Tellurium Recovery

1. Function - The processing solutions which have become rich in selenium and tellurium are treated in laboratory-scale equipment to recover these elements as by-products (1). Both are valuable for use in manufacture of electrical and electronic products, and in xerographic copying machines.

The alkaline solutions are made acidic with sulfuric acid to a pH of 5.5 to 6.5 (2,3). Tellurous acid (H_2TeO_3) precipitates, and is removed by filtration. Then the solution is treated by bubbling SO_2 through it. Selenium and any remaining tellurium precipitate in elemental form, and can be selectively separated by several stages of precipitation and filtration. Both are dried to become marketable products, or they may be further purified prior to sale.

The crude tellurous acid is dissolved in caustic, treated with sodium sulfide to precipitate impurities, and filtered. The clear solution is again acidified, and the pure tellurous acid again precipitates. When filtered and dried, it can be sold in this form or may be further processed to elemental tellurium.

A number of purification and reduction processes are used to produce pure materials. All are very small-scale operations.

Only a very small percentage of the tellurium in the original copper ore is reclaimed. Ninety percent is lost during ore flotation, while in each subsequent processing step, from 20 to 60 percent of the tellurium that remains is lost (4). Selenium recovery is reported to be much higher - recovery of 80 percent, with the remainder lost to slags, flue dusts, and gases (4).

2. Input Materials - The principal input is the filtered solution from soda slag leaching (Process No. 28), to which are added selenium and tellurium extracted or floated from scrubber precipitates (Process No. 27).

Laboratory-grade reagents are normally used, such as sulfuric acid, sodium hydroxide, compressed and liquified SO_2, and others. Quantities are very small.

3. Operating Conditions - Temperatures may reach 450°C during some purification steps. Pressures are normally atmospheric.

4. Utilities - A variety of laboratory utilities may be employed. Consumption of each is negligible.

5. Waste Streams - No gas or solid wastes are generated by this process in anything other than trace amounts.

Liquids are low in volume and normally discharge through standard laboratory waste systems.

6. Control Technology - None applicable

7. EPA Source Classification Code - None

8. References -

1. Leigh, A.H. Precious Metal Recovery Practice International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

2. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

3. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

4. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Doré Metal Separation

1. Function - In a series of complex chemical and electrochemical laboratory operations, the Doré metal, a mixture primarily of silver, gold, and the platinum group metals, is separated into specification grades of each of these metals (1).

A special small electrolytic cell, the Moebius cell, is used to separate the silver, which is further processed to produce bullion bars, analyzed at 99.97 percent silver, of 1000 troy ounces each (2,3).

Mud from the Moebius cell is melted into anodes and processed in another special electrolytic device, the Wohlwill cell, which produces gold of marketable quality.

The remaining electrolyte is chemically processed to separate platinum, palladium, and occasionally other metals. Iridium, rhodium, ruthenium, and others may be present.

2. Input Materials - The principal input is Doré metal (see Process No. 26).

Small quantities of many inorganic chemicals are used. The list includes sulfuric, nitric, and hydrochloric acids, powdered iron and copper metals, and sulfur dioxide.

3. Operating Conditions - Temperatures during the various steps of processing range up to 1300°C in the casting of the metals, but most operations are at less than 100°C. No unusual laboratory pressures are employed.

4. Utilities - Electricity is used for the electrochemical operations, and either electricity or gas for operation of the casting furnace. Utility consumption is negligible in comparison with other processes in this industry.

5. Waste Streams - No losses of unusual metallic elements occur in this process. There are minor evolutions of nitrous oxides, sulfuric acid mists, and other acid fumes, and occasional liquid discharges of electrolyte acids in quantities of a few gallons at most. No solid wastes are produced, although residues may occasionally be returned to the Doré furnace.

6. Control Technology - Local ventilation is the only control exercised for this process.

7. EPA Source Classification Code - None

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Primary Copper Smelting Subcategory and the Primary Copper Refining Subcategory of the Copper Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA 440/1-75/032-b. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Leigh, A.H. Precious Metal Refining Practice the International Symposium on Hydrometallurgy. Chicago, Illinois. February 25 - March 1, 1973. pp. 95-110.

Vat Leaching

1. Function - Vat leaching is a simple form of hydrometallurgy in which copper is dissolved from oxide ores to form aqueous solutions. The leaching takes place in an arrangement of tanks or vats.

Oxidized copper minerals, occurring as partially weathered deposits in the mine, cannot easily be processed by conventional smelting processes. These deposits are selectively mined and crushed to about 1 to 1.25 centimeters (1). The crushed ore is then placed in concrete vats of up to 18,000 metric tons capacity, and subjected to alternate flooding with sulfuric acid and draining. After the copper oxides are converted to soluble copper sulfate, the remaining soluble copper is removed by a countercurrent wash of fresh water. The vat floor is a filter which facilitates upflow and downflow of wash and leach solutions. The resulting solutions are too dilute for electrowinning; they are usually treated by cementation (Process No. 33) or solvent extraction (Process No. 34) (1).

One proprietary process has been developed for vat leaching of a roasted sulfide ore in which the sulfide ore is converted into sulfates prior to hydrometallurgical processing (see Process No. 36).

Vat leaching is similar in principal to the leaching of sulfide ores (Process No. 32), but the vat leaching operations are usually more carefully controlled and result in lower potential for damage to the environment. Vat leaching is the most efficient process yet developed for the recovery of copper values from oxidized copper minerals.

2. Input Materials - The principal input is the oxide ore material, as described above.

Sulfuric acid has been the only solvent used for simple leaching since it is not only inexpensive and nonvolatile, but also has a slight selective action for copper. Consumption will vary, but extraction of a metric ton of copper from a 1 percent ore body containing oxidized minerals will require about 4400 liters of 96 percent acidity (2).

3. Operating Conditions - The process operates at atmospheric pressure and ambient temperatures.

4. Utilities - Diesel fuel and electricity are used in the materials handling operations, and electricity in pumping the leach solution. Process water must be added to most of these operations, since in this country they are located in arid regions with high evaporation losses. In 1973 water usage was 50 to 200 cubic meters per metric ton of copper precipitate (2).

5. Waste Streams - Vat leaching produces a large amount of tailings of waste rock that is sluiced into a tailings pond. This material is comparable with the waste from a concentrator plant (Process No. 2). Frequently the same pond is used for both concentrator and vat-leaching tailings.

The circulating stream of a leaching operation may become so rich in impurities that it must be discarded. No analyses have been reported; the volume is reported as varying from 350,000 to 1,000,000 liters of spent liquor per metric ton of copper produced (3).

6. Control Technology - Most installations mix the discharge of this process with mining or concentrating wastes. Control is described in connection with Process No's. 1 and 2.

7. EPA Source Classification Code - None

8. References -

1. Williams, Roy E. Waste Production and Disposal in Mining, Milling and Metallurgical Industries. Miller Freeman Publications, Inc. San Francisco. 1975.

2. Roberts, R.W. San Xavier Vat Leach Plant Operation. Mining Congress Journal. December 1974.

3. Davis, W.E. National Inventory of Sources and Emissions: Copper, Selenium, and Zinc. PB 210-677, 678, and 679. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. May 1972.

Sulfide Ore Leaching

1. Function - Heap and dump leaching are simple forms of hydrometallurgy in which copper is dissolved from sulfide ores to form aqueous solutions. In heap leaching, the ore is placed in a pile on the ground. In dump leaching, the overburden and low grade waste from the mine are leached in the dumps formed during the mining operation. In situ and thin layer leaching may also be utilized for sulfide ores.

This process is an accelerated form of natural weathering. It is usually applied to low-grade ore that contains less than 0.4 percent copper (1,2,3). Material is placed in an area provided with drainage ditches and basins, and is alternately flooded with sulfuric acid solution and allowed to drain. This procedure causes rapid oxidation of the copper minerals. Soluble copper sulfate is formed, and washes from the heap with the acid solution. From 70 to 82 percent of the copper in these low-grade ores can be recovered (3,4). The liquor that seeps from the heap has a pH of 1.5 to 2.5 (5) and may contain from 1.0 to 18 grams of copper per liter (4,5).

In the leaching of sulfide ores, barren solutions of sulfuric acid from a copper cementation process are applied originally, after which only makeup water is required periodically to sustain the leaching process. Water and oxygen react with pyrite in the dump to generate sulfuric acid and ferric sulfate; this solution effectively dissolves the copper present. If the ores contain significant amounts of oxides or carbonates, sulfuric acid must be added periodically. A dump leaching site is characterized by a grid of ponds that collect the pregnant leach liquor (6).

In situ leaching involves breaking the ore in place and alternately circulating air and leach solution through the fractured material. The pregnant liquor is collected in a system of tunnels.

A recent modification of sulfide ore leaching is the "thin layer" process, in which still further acceleration of the weathering reactions is brought about by spreading the ore thinly over a large surface area. This modification is in use in South America, but has not been reported to be in use in this country.

These techniques of hydrometallurgy allow the extraction of copper from low-grade ores without evolution of sulfur dioxide. These can be small operations that require less capital expenditure than pyrometallurgical processing. The overall cost to produce a ton of copper is greater, however, and there is no way in simple leaching to recover the precious metals content of the ores.

2. Input Materials - The principal input is the ore materials, as described above. In most cases, these would otherwise be waste materials, unprofitable to process by conventional techniques.

Sulfuric acid is the leaching chemical. To some extent, leaching operations are practiced as a means for disposition of excess smelter acid. Consumption will vary and will depend largely on the composition of the gangue rock. If there is no limestone in the gangue, very little acid is consumed.

3. Operating Conditions - Since the process occurs in an open, outdoor area, it operates at atmospheric pressure and ambient temperatures.

4. Utilities - Diesel fuel and electricity are used in the materials handling operations, and electricity in pumping the leach solution. Process water must be added to most of these operations, since in this country they are located in arid regions with high evaporation losses. In 1973, water usage in heap leaching ranged from 920 to 4850 cubic meters per metric ton of crude copper precipitate produced (4).

5. Waste Streams - Wastes from heap leaching include fugitive dusts from materials handling, and quantities of highly mineralized solid wastes containing residual sulfuric acid. It is usually difficult to separate these wastes from those of the mining process, as discussed in more detail in Process No. 1.

The circulating stream of a leaching operation may become so rich in impurities that it must be discarded. No analyses have been reported; the volume is reported as varying from 350,000 to 1,000,000 liters of spent liquor per metric ton of copper produced (7).

6. Control Technology - Most installations mix the discharge of this process with mining or concentrating wastes. Control is described in connection with Process No's. 1 and 2.

7. EPA Source Classification Code - None

8. References -

1. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

2. Copper Hydrometallurgy: The Third-Generation Plants. Engineering and Mining Journal. June 1975.

3. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

4. Roberts, R.W. San Xavier Vat Leach Plant Operation. Mining Congress Journal. December 1974.

5. Gardner, S.A. and G.C.I. Warwick. Pollution-Free Metallurgy: Copper via Solvent-Extraction. Engineering and Mining Journal. April 1971.

6. A Study of Waste Generation, Treatment and Disposal in the Metals Mining Industry. PB-261 052. U.S. Environmental Protection Agency, Washington, D.C. October 1976.

7. Davis, W.E. National Inventory of Sources and Emissions: Copper, Selenium, and Zinc. PB-210 679, PB-210 678, and PB-210 677. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. May 1972.

Cementation

1. Function - The cementation process converts soluble copper into a metallic precipitate through chemical reaction with metallic iron. It is used to recover copper from strong solutions created by other processes, especially those from heap and vat leaching.

This process is dependent upon the relative activity of a metal to become a soluble ion. Metals can be listed in a continuous electromotive series; iron, having higher activity, will preferentially replace a copper ion in solution and thus produce an insoluble precipitate, often called "cement copper". In a typical application, liquor draining from a heap leaching operation flows through a trough that is filled with scrap iron. Part of the copper precipitates, and the liquor is recycled back to the heap. It is reported that 94 percent of the copper can be recovered by this method (1,2).

Periodically, the trough is cleaned and the cement copper is sent to a smelter for processing. The cement copper is usually a mixture of copper with iron compounds and other insoluble minerals. The copper content is generally around 70 percent and is rarely more than 90 percent (1,3).

In many of its applications, cementation is being replaced by solvent extraction and electrowinning techniques (see Process No's. 34 and 35).

The term cementation is also applied in this industry to other similar chemical reactions. Zinc metal is used in cementation of gold and copper, and copper powder is used in cementation of silver (4).

2. Input Materials - Aqueous liquors containing dissolved copper are the principal input. The process is efficient only with fairly concentrated solutions.

Scrap iron is most commonly used for cementation if it can be obtained. Because it is becoming difficult to obtain sufficient scrap of good quality, a process for manufacture of a sponge iron is in the final steps of development (see Process No. 37).

3. Operating Conditions - Cementation processes normally operate at atmospheric pressure and ambient temperatures.

4. Utilities - No utilities are consumed unless special pumps are required to cause the liquor to flow through the cementation tanks.

5. Waste Streams - Atmospheric pollution from the cementation process is negligible. There may be tiny amounts of hydrogen gas created by a side reaction of acid with the iron.

No liquid wastes can be directly assigned to this process when used as an auxiliary to a larger liquid handling operation. In the case of a separate operation, analysis of a typical treated leach liquor is presented below in Table 38.

TABLE 38. ANALYSIS OF TAILINGS EFFLUENT
FROM A PRECIPITATION PLANT (5)

Parameter	Maximum, mg/l	Minimum, mg/l	Average, mg/l
Sulfate	53,000	33,000	38,882
Copper	76.3	27.7	52.2
Iron	3100	2050	2632
Lead	0.92	0.05	0.67
Mercury	0.0006	0.0001	0.0003
Selenium	0.95	0.01	0.12
Zinc	146	129	136

Solid waste resulting from cementation includes scrap iron partially used, discarded, or abandoned, causing some of these operations to resemble a junk yard.

6. Control Technology - No controls are specific to this process.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Roberts, R.W. San Xavier Vat Leach Plant Operation. Mining Congress Journal. December 1974.

3. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. October 1974.

4. Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry. Point Source Category, Volumes I and II. EPA/1-75/032-6. U.S. Environmental Protection Agency. Washington, D.C. February 1975.

5. Personal Communication with J.V. Rouse, U.S. Environmental Protection Agency. National Enforcement Investigations Center. Denver, Colorado. 1976.

Solvent Extraction

1. Function - As applied in the copper industry, solvent extraction is a method to produce a concentrated copper solution, relatively free of other metal ions, from a solution of copper that does contain other dissolved metals. The process uses a special mixture of organic solvents in an agitated vessel. When the solvents are mixed with the impure solution, the copper combines with the solvents as a complex. Agitation of the vessel is then stopped and the solvents, now containing the copper, form a separate layer. The water layer is drained off. Sulfuric acid is then mixed with the solvent. This breaks down the complex and regenerates the solvent for reuse. The copper is withdrawn as a solution in the acid.

Solvent extraction has been applied to liquors from vat leaching, and it is being incorporated into some of the developing hydrometallurgical processes (1). The concentrated acid solution can be directly treated by electrowinning (see Process No. 35). This process can also be made continuous, rather than batch, to adapt it to large-scale operations.

It is reported that about 95 percent of the copper in a solution can be extracted by this technique (2).

2. Input Materials - Water solutions of copper are the primary input. There is no published information on the composition ranges that can be efficiently treated with this process.

The solvents mixture is kerosene containing about 12 percent of a proprietary chemical made by General Mills called LIX (3,4). The total rate of recycle is not known, but losses of 0.1 liter per 1000 liters of impure solution have been reported (4). Two other chemicals, "Kelex" and "Shell 529," are also being advertised for this application.

Concentrated sulfuric acid is required (normally recycled through electrowinning cells), but quantities have not been reported.

3. Operating Conditions - No special temperature limits are reported; it is assumed that ambient temperatures and atmospheric pressure are satisfactory.

4. Utilities - A small amount of electricity is required for agitation and liquid pumping.

5. Waste Streams - There are no reports of atmospheric pollution from this process. For operating safety, evaporation of the solvent is undoubtedly minimized.

The manufacturer of the LIX solvent states that small amounts of iron, arsenic, and zinc are extracted along with the copper (1). The procedure for disposal of these materials has not been reported. It is likely that there will be a bleed of the concentrated acid to prevent accumulation of these other elements.

The loss of solvent is reported as 1 liter per 10,000 liters of raffinate (2). It is likely that this is almost entirely kerosene, which has a slight water solubility. The more expensive chelating compounds should stay largely dissolved in the kerosene layer. No confirmation of this has been published.

No solid wastes are generated by this process.

6. Control Technology - No special controls are indicated. The possible acid blowdown should be of a quality that could be reused in other processes. The organic loss would be biodegradable if this waste stream were combined into other wastewaters.

7. EPA Classification Code - None

8. References -

1. In Clean-Air Copper Production, Arbiter is First off the Mark. Engineering and Mining Journal. 1973.

2. Gardner, S.A. and Warwick, G.C.I. Pollution-Free Metallurgy: Copper via Solvent-Extraction. Engineering and Mining Journal. April 1971.

3. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

4. Ion Exchange: The New Dimension in Copper Recovery Systems. Engineering and Mining Journal. June 1975.

Electrowinning

1. Function - Electrowinning is a process for the extraction of relatively pure copper metal from a solution containing copper ions. This is an electrolytic process, similar to the cells of an electrolytic refinery (see Process No. 19), except than an inert anode is used. Copper metal deposits at the cathode, and the water in the solution is electrolytically decomposed, liberating oxygen at the cathode, and regenerating the sulfate ion as sulfuric acid.

If the copper solution is relatively pure, the copper produced by electrowinning is comparable with the best electrolytic copper, assayed as 99.9 percent plus (1). If impure solutions direct from vat leaching are used, the purity is equivalent to that of the anode copper from a conventional smelter and the product thus requires electrolytic refining prior to sale.

2. Input Materials - Electrowinning is in use to recover copper directly from vat leaching solutions (Process No. 31), and from purified solution from solvent extractions (Process No. 34). It is also being tested as a part of some of the more sophisticated hydrometallurgical processes that are being developed, in which chlorides rather than sulfates will be the input materials (see Process No. 38) (2).

Additives to produce a uniform cathode deposit are necessary. They are the same as for electrolytic refining. One report lists glue for electrowinning being added at a rate of 0.02 to 0.06 kilogram per metric ton of cathode copper (3).

3. Operating Conditions - Electrowinning cells are maintained at about 60° to 65°C and at atmospheric pressure (2,3).

4. Utilities - Electrowinning requires 8 to 10 times as much electric current as does an electrolytic refining cell to produce the same amount of copper (3). In a loop with a solvent extraction process, 2.44 kilowatt-hours are required to produce a kilogram of copper (4). In direct electrowinning of a vat or heap leach solution 2.79 kilowatt-hours per kilogram of copper are required (3). These high values reflect the energy required to dissociate water into its elements and are the principal reason that the simple hydrometallurgical processes have been more expensive than conventiona smelting.

A small amount of water is used to clean the cathodes after removing them from the cell.

5. Waste Streams - The oxygen produced at the anode of an electrowinning cell can be considered either as an atmospheric emission or as a by-product. If it is discarded to the atmosphere, there are no deleterious environmental effects.

A small amount of liquid waste may be discharged in connection with cleaning of the completed cathodes. No reports of this source have been published.

The possible larger purge of electrolyte, necessary to prevent accumulation of other elements, was discussed in connection with Process No's. 31, 32, and 34.

There are no solid wastes from this process.

6. Control Technology - No special controls are applicable to the wastewater that may develop from this process.

7. EPA Source Classification Code - 3-03-005-0

8. References -

1. Gardner, S.A. and Warwick, G.C.I. Pollution-Free Metallurgy: Copper via Solvent-Extraction. Engineering and Mining Journal. April 1971.

2. Atwood, G.E., and Curtis, C.H. Hydrometallurgical Process for the Production of Copper. U.S. Patent No. 3,785,944. January 15, 1974.

3. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

4. Ion Exchange: The New Dimension in Copper Recovery Systems. Engineering and Mining Journal. June 1975.

Sulfation Roasting

1. Function - One company has developed a hybrid process that will use a fluidization roaster (Process No. 4) to prepare a calcine especially suited to vat leaching (Process No. 31). This is the technique of sulfation roasting. In this process, concentrate is roasted to oxidize the copper to copper sulfate and the iron to iron oxide, and to remove the excess sulfur as sulfur dioxide. Roasting is a batch rather than a continuous operation.

2. Input Materials - This plant will use an ore concentrate that is predominantly chalcopyrite ($CuFeS_2$) (1). It is expected that any sulfide concentrate could be used. The concentrate is blended with Fe_2O_3, which moderates the heat produced by the exothermic oxidation reaction and promotes sulfation of the copper. A ratio of two parts concentrate to one of iron oxide is believed to be about optimum (2).

3. Operating Conditions - Temperatures are kept much lower than in conventional roasting. Instead of 760°C, the range is 400° to 600°C (2,3). Pressures are approximately atmospheric.

4. Utilities - Gas or oil is used to preignite the charge and to maintain temperature.

Noncontact cooling water is used to regulate temperatures of the roaster.

Air or oxygen is injected through the bottom of the charge for oxidation. Twenty percent above theoretical amount of oxygen will be required for the duration of each batch (2).

5. Waste Streams - It is believed that emission of metallic fumes will be considerably less than in a conventionally operated roaster. Particulate emissions following the roaster cyclones have not been estimated.

Organic flotation reagents are expected to be volatilized into the exit gases and oxidized. The gas stream is expected to contain 8 percent SO_2 and 4 percent oxygen (4). Gas temperature should be less than 400°C.

There will be no solid or liquid wastes from this process.

6. Control Technology - A 225 metric ton per day single-contact sulfuric acid plant will remove from 70 to 80 percent of the SO_2 from this process (4,5). This operation will require complete particulate removal, but it is not known what devices will be used.

7. EPA Source Classification Code - 3-03-005-02

8. References -

1. Haver, F.P. and M.M. Wong. Lime Roast-Leach Method for Treating Chalcopyrite Concentrate. U.S. Bureau of Mines, Washington, D.C. 8006. 1975.

2. Foley, R.M. Method of Treating Copper Ore Concentrates. U.S. Patent No. 2,783,141. February 26, 1957.

3. Haskett, P.R., D.J. Bauer, and R.E. Lindstrom. Copper Recovery from Chalcopyrite by a Roast-Leach Procedure.

4. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. EPA-450/2-74-002a. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

5. Potter, J. Personnal Communication on Hydrometallurgical Processes. Bureau of Mines. Salt Lake City, Utah. 1976.

Sponge Iron Plant

1. Function - One company is building a sponge iron plant to accompany its sulfation roasting installation (Process No. 36)(1). After leaching the copper from the calcine produced by sulfation roasting, the leach residue contains mostly iron oxide plus smaller amounts of copper and precious metals. This process will partially reduce the iron, which will then be used for cementation of liquor from the vat leaching of oxidized copper ores. The precipitate from this process is expected to contain the precious metals from the concentrate originally fed into the sulfation roaster (2), and will therefore provide a means of recovery.

The sponge iron will be produced in a kiln by reduction with coal. The iron is not to be high-purity grade, but will be adequate for cementation.

2. Input Materials - The principal input is the residue from vat leaching of sulfation roasted concentrates.

Coal is to be used in the proportion of one ton of coal for each two tons of sponge iron produced.

3. Operating Conditions - Kiln temperatures are expected to be approximately 1100°C (3). Pressures are approximately atmospheric.

4. Utilities - Gas or oil is used to heat the charge until the coal is ignited, and is then used only if required to maintain temperature.

Combustion air is allowed to enter the kiln in carefully regulated amounts. Air quantity is calculated to be 1.5 tons of air per ton of iron produced (3).

5. Waste Streams - No emission data are available, since this process is not yet in operation. Particulates and fumes of volatile metals would be expected in a gas containing appreciable carbon monoxide.

There should be no liquid waste.

The process will generate a solid waste in the form of a slag.

6. Control Technology - It is not yet known what atmospheric control devices will be employed with this process.

The slag is expected to be discarded in a waste dump also used for wastes from ore concentrating operations.

7. EPA Classification Code - None

8. References -

1. Potter, J. Personal communication on Hydrometallurgical Processes. Bureau of Mines. Salt Lake City, Utah, 1976.

2. Hydrometallurgy Makes Advances in Copper Processing. Engineering and Mining Journal. 1973.

3. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

CLEAR Reduction

1. Function - An advanced hydrometallurgical process has been developed with the trade name of CLEAR (Copper Leaching, Extraction, and Refining). The descriptions for Process No's. 38 through 40 outline the three sections of this method.

The first step of the CLEAR system, called a reduction, could also be called a leaching operation. It uses as a solvent a water solution of cupric, ferrous, and sodium chlorides (1). Primarily the cupric chloride is active during this step, reacting with copper ore minerals to form cuprous chloride, additional ferrous chloride, and elemental sulfur. The sulfur is a solid material and remains with the leach residue. Since only about half the copper in the concentrate is solubilized in this first leach, it is treated a second time in the oxidation process (Process No. 40).

Although leaching of fresh concentrate does occur, the principal purpose of this step is to prepare the liquor for electrowinning. It may be reduced with other materials if necessary, then filtered and sent to electrowinning cells (2). These cells are similar to those described in Process No. 35, but are slightly modified for chloride service, operating at a slightly lower temperature, around 55°C. After electrowinning removes part of the copper, the liquor is sent to the Regeneration-Purge step (Process No. 39).

2. Input Materials - A typical Arizona ore concentrate is the primary input. Chalcopyrite is the predominant ore mineral.

The leach liquor at this stage contains about 8 percent cupric chloride, 12 percent ferrous chloride, and 13 percent sodium chloride (1). It is received directly from the oxidation leach of the previous batch (see Process No. 40).

To complete the reduction of the liquor, scrap iron or copper, sodium sulfite, or sulfur dioxide may be added (2).

3. Operating Conditions - The CLEAR process operates at higher temperatures than some other hydrometallurgical processes; 107°C has been reported (1). Pressures are atmospheric.

4. Utilities - Although there are no published reports, the source of heat is probably steam. Electricity is also undoubtedly required for materials handling and pumping.

5. Waste Streams - Some loss of hydrochloric acid vapor from a residual in the leach liquor may occur, but the leaching step is enclosed to minimize this emission. Dust may arise from materials handling.

The process generates no intentional waste streams; with the corrosive solutions, however, accidental losses of liquids are likely.

6. Control Technology - Any losses of hydrochloric acid vapors can be controlled by scrubbing with an alkaline solution.

7. EPA Classification Code - None

8. References -

1. Atwood, G.E., and C.H. Curtis. Hydrometallurgical Process for the Production of Copper. U.S. Patent No. 3,785,944. January 15, 1974.

2. Rosenzweig, M.D. Copper Makers Look to Sulfide Hydrometallurgy. Chemical Engineering. Volume 83, No. 1: pp. 79-81. January 5, 1976.

CLEAR Regeneration - Purge

1. Function - Exhausted and stripped solvent from the electrowinning cells that follow the reduction process (Process No. 38) is oxidized with air to remove excess iron and to prepare the solution for the pressurized leach operation (Process No. 40). Air is blown through the solution, and ferrous iron is oxidized to ferric chloride and ferric hydroxide. Copper in the solution acts as a catalyst for this oxidation (1). Sulfates are also formed and collect into an insoluble compound similar to the mineral jarosite (2). The jarosite and ferric hydroxide are filtered out and discarded.

2. Input Materials - Liquor from the electrowinning cells is the only input. At this stage, the solution contains about 6 percent cuprous chloride, 8 percent ferrous chloride, and 14 percent sodium chloride (3).

3. Operating Conditions - This is a pressurized process, operating at 107°C and 2.7 kilograms per square centimeter (3).

4. Utilities - Source of heat has not been reported. Either steam or direct firing could be applicable.

Compressed air is required, and process water is added at this step to compensate for evaporation and losses. Quantities are unknown.

5. Waste Streams - Although no data have been reported, a gaseous stream must be released from this step carrying hydrochloric acid vapor and steam.

Solids removed by filtration are discarded. Composition is reported to be primarily an iron sulfate/hydroxide mixture (3). Other elements leached from the concentrate will be present. The quantity of solids produced is about 2 to 4 percent of the total weight of spent electrolyte (3). Liquids will probably drain to waste from the solids.

6. Control Technology - The gas stream from this oxidation operation is undoubtedly processed to recover the vaporized and entrained materials. This is probably accomplished by external cooling, condensation, and water scrubbing. No details have been disclosed.

The solid wastes from this process are mixed with the wastes from the oxidation step (Process No. 40) and sluiced into a settling pond. In locations other than the arid region where this plant is operating, secondary water pollution could be substantial.

7. EPA Classification Code - None

8. References -

1. Potter, J. Personnal Communication on Hydrometallurical Process. Bureau of Mines. Salt Lake City, Utah, 1976.

2. Rosenzweig, M.D. Copper Makers Look to Sulfide Hydrometallurgy. Chemical Engineering. Volume 83, No. 1: pp. 79-81. January 5, 1976.

3. Atwood, G.E., and C.H. Curtis. Hydrometallurgical Process for the Production of Copper. U.S. Patent No. 3,785,944. January 15, 1974.

CLEAR Oxidation

1. Function - This is the principal leaching operation of the CLEAR system, in which partially leached ore concentrate is contacted with freshly regenerated leach solution. Primarily the ferric chloride is active during this step, reacting with copper ore minerals to form ferrous chloride, cupric chloride, and elemental sulfur.

The sulfur is a solid material that remains with the leach residue. It is reported that 98 percent of the residual copper is extracted in this step (1). The solids from this process are discarded, although cyanide treatment for gold recovery may be performed if the gold analysis warrants it (see Process No. 2).

The leach solution is filtered and sent to the reduction step (Process No. 38) (2).

2. Input Materials - Solid residue from Process No. 38 and liquor from Process No. 39 are the only input materials. The ratios have not been disclosed. The liquor at this stage contains about 6 percent cupric chloride and 15 percent each of ferric and sodium chlorides (1).

3. Operating Conditions - This is a high-temperature, pressurized leaching operation. Temperatures of 140°C and pressures of 2.7 kilograms per square centimeter are used (3).

4. Utilities - Source of heat has not been reported; either steam or direct firing could be applicable. Electricity is undoubtedly required, but again no information has been published.

5. Waste Streams - Details of the process have not been disclosed in sufficient detail to establish whether emissions of gases to the atmosphere occur. Hydrochloric acid vapors could be generated.

The major waste of the CLEAR system, consisting of the solid residue, is discharged from this step. This residue may be a large fraction of the original concentrate. It is expected to be 99 percent free of copper (1) and much reduced in iron; it must contain considerable colloidal sulfur and soluble chlorides. It may contain cyanides if gold extraction was performed. No analyses have been published.

6. Control Technology - The process will likely incorporate an operating control of hydrochloric acid emission, since even small concentrations of this very corrosive gas can damage plant equipment. If needed, scrubbing with an alkali can further reduce the concentration.

Solid wastes from this process are sluiced into a settling pond. The location of this first application is such that natural evaporation should dispose of the water content, and secondary water pollution should be minimal.

In other locations, however, this waste could cause severe secondary pollution in the form of an acidic seepage high in chlorides, sulfates, and heavy metals.

7. EPA Source Classification Code - None

8. References -

1. Atwood, G.E., and C.H. Curtis. Hydrometallurgical Process for the Production of Copper. U.S. Patent No. 3,785,944. January 15, 1974.

2. Potter, J. Personnal Communication on Hydrometallurgical Process. Bureau of Mines. Salt Lake City, Utah, 1976.

3. Rosenzweig, M.D. Copper Makers Look to Sulfide Hydrometallurgy. Chemical Engineering. Volume 83, No. 1: pp. 79-81. January 5, 1976.

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